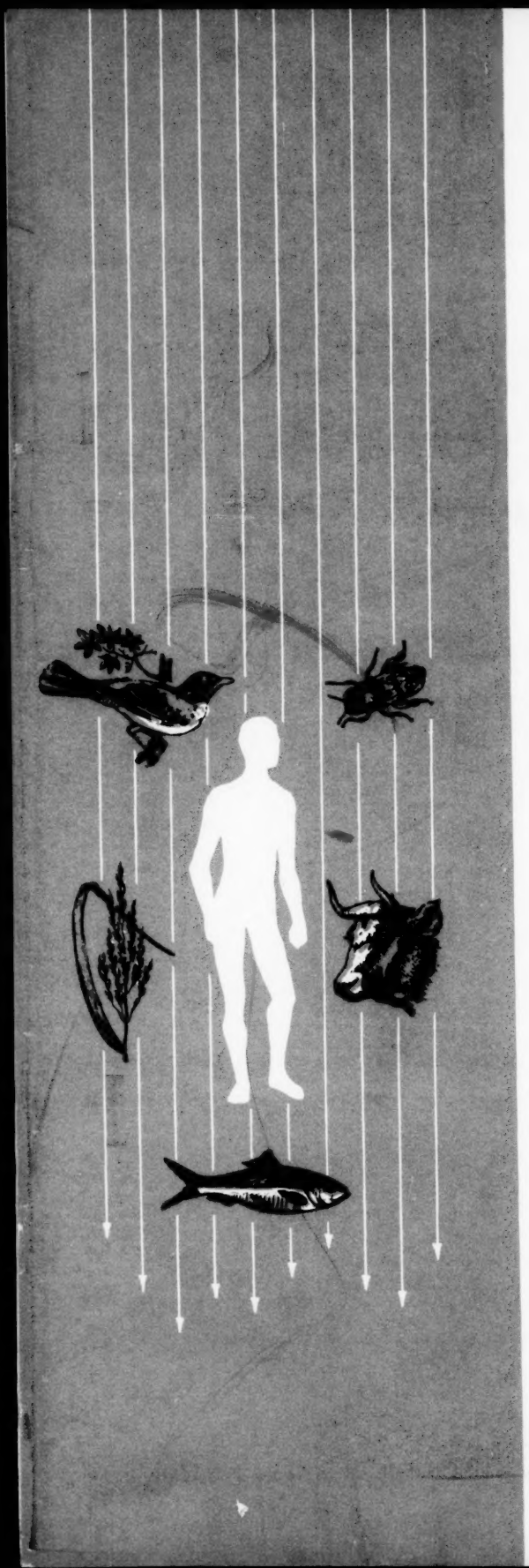

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RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Chlorinated Hydrocarbon and PCB Residues in Tissues and Lice of Northern Fur Seals, 1972 [1]

David A. Kurtz [2] and Ke Chung Kim [3]

ABSTRACT

DDT, dieldrin, and PCB contents of tissues and the sucking lice of the northern fur seal (Callorhinus ursinus) *were studied in samples collected in July 1972 in the Pribilof Islands, Alaska. They included the analyses of two nursing cows and their two newborn pups, three 2-month-old pups, and the sucking lice inhabiting these animals,* Antarctophthirus callorhini *and* Proechinophthirus fluctus. *The ΣDDT content of fat tissue was 5.2, 5.6, and 63 μg/g* ($\bar{x}$) *for cows, newborns, and 2-month-old pups, respectively. Dieldrin appeared at trace levels. PCB residues (Aroclor 1254) were 5.8, 5.5, and 33 μg/g* ($\bar{x}$)*, respectively. The ΣDDT content of blood was less than 0.01 μg/g for cows and newborns and 4.6 μg/g for 2-month-old pups. PCB's were found only in trace amounts in the blood of all animals except one 2-month-old pup which contained 3.4 μg/g. Lice contained 0.2-6 percent, respectively, of the ΣDDT and PCB's detected. All residues were expressed on a wet-weight basis. Two-month-old pups had far higher residue levels than had cows. A high percentage of* ΣDDT occurred *as the DDE metabolite: 60 percent in cows and newborn pups and 90 percent in 2-month-old pups.*

Introduction

Biological concentrations of pesticide residues in harp, harbor, gray, and ringed seals have been reported on a world-wide basis (*1-3, 8-9, 12-15, 21-25*), but they are indicators of generally localized pesticide contamination levels since these species are localized. Anas, in fact, has suggested that harbor seals could be used to locate geographical areas where organochlorine and polychlorinated biphenyl (PCB) concentrations are high (*3*).

The northern fur seals, *Callorhinus ursinus*, on the other hand, are migratory and have an open ocean habitat. They subsist solely on marine fishes and invertebrates. They spend 4-5 months on the Pribilof Islands in Alaska and the remainder in the northern Pacific Ocean ranging from the Bering Sea to areas off the coasts of California and Japan. Analysis of fur seals would thus be an indicator of pesticide concentrations of the neritic seas. Anas and Wilson have studied pesticide concentrations in 30 fur seals collected on the Pribilof Islands in 1968 and off the California cost in 1969 (*4*). ΣDDT concentrations in liver of male and female seals of all ages averaged 0.78 and 0.98 ppm, respectively; they were found in quantities of 0.21 ppm and 0.26 ppm, respectively, in samples of brain tissue. Dieldrin was detected in only three liver samples and in no brain samples. PCB's were not detected. In five samples of liver and brains from seals collected in November 1969 on the Pribilof Islands, Anas and Wilson found 2.21 ppm ($\bar{x}$) and 0.20 ppm ($\bar{x}$) ΣDDT, respectively, no dieldrin, and traces of PCB. In blubber they found 15.9 ppm ($\bar{x}$) ΣDDT, 0.045 ppm ($\bar{x}$) dieldrin, and only traces of PCB (*5*).

This paper reports the accumulation of ΣDDT, dieldrin, and PCB's in tissues and the sucking lice of the northern fur seals, *Callorhinus ursinus*. Two species of the sucking lice, *Antarctophthirus callorhini* and *Proechinophthirus fluctus*, are parasitic on the fur seal. The taxonomy, ecology, and population biology of these lice have been studied by one of the authors (*17-19*). The detection of mercury in the tissues and the sucking lice of these fur seals has also been reported by Kim et al. (*20*).

Materials and Methods

Samples of body tissue and the sucking lice were collected from the northern fur seals on St. Paul Island, Alaska, in July 1972. Fat and blood samples were taken from two nursing cows, two newborn pups, and three 2-month-old pups. Subcutaneous fat samples were taken

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from the abdominal region and blood was taken directly from the heart. Fat was collected as a single small sample. Anas and Worlund have speculated that this method produces less specific residue levels than does the collection of a larger homogenized sample (*6*).

Sucking lice of the species *A. callorhini* were collected from all five pups and those of the species *P. fluctus* were collected from only the 2-month-old pups. All samples were stored in glass vials and kept frozen from the time of collection until analysis. The two pregnant cows were caged away from the rookery for study, and samples were taken from these two nursing cows and two newborn pups in captivity for this study.

Blood samples were extracted by vortexing 50 mg with 5 ml hexane four times. Hexane layers were combined, concentrated to 1 ml, and passed through a small florisil column containing 2.3 g florisil. Lice and fat samples were ground in a Duall tissue grinder, size B. Lice samples generally varied from 8 to 29 mg; for one 2-month-old pup the *P. fluctus* sample was 139 mg. Fat samples weighed 200 mg. Each sample was extracted three times with 3 ml acetonitrile each time. The combined acetonitrile layers were extracted once with 5 ml hexane to remove excess fats. To the remainder was added 9 ml water containing 1 percent sodium sulfate and this solution was then extracted three times with 3 ml hexane. The hexane layers were combined, concentrated, and passed through a florisil column containing 2.3 g activated florisil. All solvents were from Burdick and Jackson and were used without further purification. The extraction and cleanup methods follow those of the U.S. Environmental Protection Agency (*26*).

Quantitative gas-chromatographic (GC) analysis was accomplished using a 160-cm U column of 1.5 percent SP-2250/1.95 percent SP-2401 on 100/120 Supelcoport packing. A Microtek 220 gas chromatograph was operated at an oven temperature of 215°C, the inlet was operated at 240°C, and the detector at 330°C. The flow of nitrogen was 60 ml/min with 20 ml/min detector purge. The electrometer sensitivity was 1.6×10^9 amp amplitude full scale.

Silicic acid column separations were run on all samples that showed residues greater than trace levels in order to separate PCB compounds from DDT compounds (*7*). Determinations were confirmed on a 155-cm column of 3 percent DEGS on 80/100 mesh Chromosorb WHP. This column was operated at 200°C, the inlet was operated at 240°C, and the detector at 330°C.

The range of recovery of DDT and metabolites was 55 to 66 percent from seal fat tissue and 56 to 58 percent from blood. The low recoveries from fat tissue were a direct result of an additional partitioning in the extraction steps. Following the original partitioning of the fat with acetonitrile, a second partitioning was performed from the acetonitrile portion with a carefully measured volume of hexane. In this step most of the lipids that were partitioned into the acetonitrile layer then moved into the hexane layer. Concurrently, smaller portions of the DDT metabolites and Aroclor mixtures were partitioned into the hexane layer and were subsequently lost from the recovery as this hexane layer was discarded. Aroclors were also recovered in a similar range, 47 percent from fat and 40 percent from blood. Other recovery data from this laboratory indicated that these data are consistent. Although massive amounts of DDT and metabolites were used for recovery, other data based on much lower added values have shown similar recovery percentages.

Results

The DDT content in fat tissues of the northern fur seals was approximately equal in cows and their newborn pups: total *p,p'*-DDT's were 5.2 μg/g and 5.6 μg/g, respectively (Table 1). Two-month pups selected ran-

TABLE 1. *Pesticide and Aroclor 1254 content in fat samples of the northern fur seal,* Callorhinus ursinus, *1972*

	Residue, μg/g wet weight							
Seal	Aroclor 1254	Dieldrin	*o,p'*-TDE	*o,p,'*-DDT	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	Sum, *p,p'*-DDT's
Nursing cow #2	6.8	0.16	0.4	1.5	3.8	1.0	2.2	7.0
Newborn pup #2	3.8	0.12	0.2	1.0	3.3	0.6	1.4	5.3
Nursing cow #3	4.7	0.07	0.1	0.6	2.0	0.4	0.9	3.3
Newborn pup #3	7.2	TR	0.3	1.0	3.9	0.6	1.3	5.8
Mean								
Cows	5.8	0.12	0.3	1.1	2.9	0.7	1.6	5.2
Pups	5.5	0.06	0.3	1.0	3.6	0.6	1.4	5.6
Pup (2 mo.) #13	16	ND	TR	0.6	98	4.7	3.1	106
Pup (2 mo.) #14	81	TR	TR	2.0	70	3.3	3.2	77
Pup (2 mo.) #15	1.3	TR	ND	TR	5.1	0.1	0.1	5.3
Mean	33	TR	TR	0.9	58	2.7	2.1	63
Recovery from 0.200 g fat sample (nursing cow #3)								
Added, ng	10^5		2000	1500	2000	2000		
Recovered, %	47		51	55	66	60		

NOTE: Analyses for all residues except dieldrin and *o,p'*TDE were corrected for recovery.
TR = trace (approximately 0.01 μg/g).
ND = no detectable residue (< 0.003 μg/g).

domly, however, had a much higher ΣDDT content. One sample contained only 5.3 μg/g ΣDDT, but the other two had 77 μg/g and 106 μg/g. The average of the three samples was 63 μg/g. The predominant DDT metabolite was DDE which accounted for approximately 60 percent of the total DDT in cows and newborns and over 90 percent in the two-month pups. The difference in the proportion of these isomers between the cows/newborns and the pups may have significance, but the sample size was too small to form any solid conclusions. It may also be significant that although small amounts of *o,p'*-DDT were found, no *o,p'*-DDE occurred in any samples.

PCB's were also found in these samples (Table 1). General GC peak patterns were seen for Aroclor 1254 but none appeared for Aroclor 1242 nor Aroclor 1260. Differential metabolism of the PCB compounds was also noted. The quantitative level found in the fat of most samples revealed that the PCB level was approximately equal to that of total *p,p'*-DDT. The average PCB level in cows was 5.8 μg/g; the average ΣDDT level was 5.2 μg/g. For the newborn, PCB's averaged 5.5 μg/g and DDT averaged 5.6 μg/g. Average PCB residue for one pup was 91 μg/g: ΣDDT averaged 77 μg/g. The Aroclor 1254 content of the other two pups was lower than the ΣDDT content: 16 μg/g vs. 106 μg/g and 1.3 μg/g vs. 5.3 μg/g.

In a recent study by Jones et al. (*16*) the blubber from one newborn fasted harp seal taken from the Gulf of St. Lawrence in 1973 contained amounts of biocide (1.47 ppm ΣDDT and 1.80 ppm PCB's) similar to those in pups who were 8-14 days old: 1.21 ppm ΣDDT and 0.9 ppm PCB's, respectively. The pups' mothers contained 4.41 ppm ΣDDT and 6.1 ppm PCB's. As in fur seals, the biocides passed the placental barrier, though in smaller amounts.

Dieldrin occurred in almost all samples in trace or very low amounts.

Levels of DDT and PCB's in the blood of these animals (Table 2) were much lower than in the fat. Absolute levels of DDT metabolites were not detectable in the cows and newborn, eliminating comparisons. The 2-month-old pups had low ΣDDT values, with a mean of 4.6 μg/g. In two samples ΣDDT was 1-3 percent of that in the fat. In the third sample results were anomalous.

PCB's occurred in blood samples only at a trace level. This suggests that, like DDT, PCB's in the blood do not exceed 3 percent of the PCB's in fat.

Lice inhabiting the bodies of the seals were analyzed; results appear in Table 3. DDT appeared in the low ppm range in lice on the 2-month-old pups. Total *p,p'*-DDT's averaged 4.4 μg/g in *A. callorhini* and 3.6 μg/g in *P. fluctus*. No quantities greater than trace were found in lice of cows or newborns. This amounts to about 6 percent of that found in fat and twice that in blood.

PCB levels in lice were generally about one-fourth of the ΣDDT levels or in the low ppm range. In the 2-month-old pups PCB's averaged 2.0 μg/g and 0.9 μg/g for *A. callorhini* and *P. fluctus*, respectively. ΣDDT and PCB's appeared in equal proportions in *A. callorhini* and *P. fluctus* species. In essentially all cases the level in the *A. callorhini* species just slightly exceeded that in the *P. fluctus* species.

Correlation coefficients for blood-lice and lice-lice relationships determined for the 2-month pups were all highly positive. Blood to *A. callorhini* lice for DDE and the sum of *p,p'*-DDT were 0.93 and 0.92, respectively. Blood to *P. fluctus* lice for DDE and the sum of *p,p'*-DDT were both 0.96. The correlations of *A. callorhini* to *P. fluctus* for PCB's, DDE, and the sum of *p,p'*-DDT were 0.69, 0.99, and 0.99, respectively.

Discussion and Conclusions

The higher ΣDDT and PCB levels of these seals compared with those collected in 1969 (*5*) indicate that

TABLE 2. *Pesticide and Aroclor 1254 content in blood samples of the northern fur seal,* Callorhinus ursinus, *1972*

	Residue, μg/g wet weight							
Seal	Aroclor 1254	Dieldrin	*o,p'*-TDE	*o,p'*-DDT	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	Sum, *p,p'*-DDT's
Nursing cow #2	TR	0.02	ND	ND	ND	ND	ND	ND
Newborn pup #2	TR	0.02	ND	ND	ND	ND	ND	ND
Nursing cow #3	TR	0.02	ND	ND	ND	ND	ND	ND
Newborn pup #3	TR	0.02	ND	ND	TR	ND	ND	ND
Pup (2 mo.) #13	TR	0.07	ND	ND	2.8	0.2	TR	3.0
Pup (2 mo.) #14	TR	0.06	ND	ND	0.6	0.1	TR	0.7
Pup (2 mo.) #15	3.4	0.05	ND	ND	10	0.3	0.1	10
Mean		0.06			4.5	0.2		4.6
Recovery from 0.05 g blood sample (nursing cow #2)								
Added, ng	4000		400	300	400	400		
Recovered, %	40		58	58	56	57		

NOTE: Analyses were corrected for recovery.
TR = trace (approximately 0.03 μg/g for DDT isomers and 0.3 μg/g for Aroclor 1254).
ND = no detectable residue (< 0.01 for DDT isomers and < 0.1 μg/g for PCB).

TABLE 3. *Pesticide and Aroclor 1254 content in sucking lice samples of the northern fur seal,* Callorhinus ursinus, *1972*

Seal	Lice[1]	Residue, μg/g wet weight						
		Aroclor 1254	Dieldrin	*o,p'*-DDT	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	Sum, *p,p'*-DDT's
Newborn pup #2	Ac	TR	TR	ND	TR	ND	TR	TR
Newborn pup #3	Ac	TR	TR	ND	TR	ND	TR	TR
Pup (2 mo.) #13	Ac	0.5	TR	ND	1.9	ND	TR	1.9
	Pf	0.4	TR	TR	1.3	0.01	0.01	1.3
Pup (2 mo.) #14	Ac	2.4	TR	TR	2.9	0.06	0.05	3.0
	Pf	TR	TR	ND	1.7	ND	TR	1.7
Pup (2 mo.) #1	Ac	3.0	TR	TR	8.2	0.04	0.06	8.3
	Pf	2.2	TR	ND	7.9	ND	TR	7.9
Mean	Ac	2.0			4.3	0.03	0.03	4.4
	Pf	0.9			3.6	0.00	0.00	3.6

NOTE: Analyses were not corrected for recovery.
TR = trace (approximately 0.01 μg/g for DDT isomers and 0.4 μg/g for Aroclor 1254).
ND = no detectable residue (< 0.003 μg/g for DDT isomers and < 0.1 μg/g for PCB).
[1]Ac = *Antarctophthirus callorhini* and Pf = *Proechinophthirus fluctus*.

the levels of pesticide residues have increased in the oceans in the past several years. Woodwell et al. (*27*) and Cramer (*10*) have proposed global models for DDT in the biosphere. In these models they discussed the various reservoirs and rates of exchange between them. The shallow seas form the last accessible reservoir before DDT which, adsorbed to organic matter, sinks to the ocean abyss. While differing in some aspects of the models, both authors predicted a maximum DDT concentration in the shallow seas in 1971-72.

Because the northern fur seal spends most of its life in the shallow portion of the northern Pacific Ocean, analysis of this animal could be a good test of the validity of Woodwell and Cramer's global DDT model. Samples in the present study were collected at the proposed peak level and, though very few in number, had higher residues than had earlier analyses. The small sampling and wide variability between samples detract from their value in confirming this theory. Further analysis of fur seals seems warranted.

Analyses also indicated that 2-month-old nursing pups had far higher levels than had cows analyzed from the same herd. The diet at this age is predominantly mother's milk (*11*), which contains as much as 50 percent fat (*5*). This implies a tremendous potential for containment of DDT. The mother herself feeds principally on small fishes and squids (*4*) whose biological loading potential is not so great as seal milk.

This magnification was not evident in the results of Frank et al. in studying harp seals (*12*). On the contrary, their data indicated that the young had lower concentrations than had adult females. Two age groups of young contained 2.1 ppm (n=19) and 2.6 ppm (n=10) ΣDDT. Adults from that area and year, however, contained 7.1 ppm (n=13). In the study of harp seals by Jones et al. similar results were obtained (*16*).

Several factors could explain the differences in results of the harp seal studies and the present authors' fur seal studies. These include the amount of biocide excreted in the milk and the degradation pathways in the seal. Little is known of the levels of biocide excreted by mother harp or fur seals in milk. Fur seal pups after 2 months of suckling ought to have higher levels than harp seal pups after only 2 weeks of feeding providing that other factors, such as the levels in the milk, amount of milk ingested, and body fat contents of the seal body, are similar. Degradation rates and pathways for these biocides in either species are not well known. Harp seals may have a higher rate of DDA formation, which has not been studied, resulting in lower DDT levels than those of fur seals. On the other hand one cannot overlook the possibility that since only two of the three nursed fur seal pups in the present study contained high DDT levels, these could have resulted from feeding from mothers who had unusually high levels themselves.

Another major finding of this study is the high percentage of degradation of the parent DDT molecule to the DDE metabolite. In both cows and newborns, 60 percent of the ΣDDT in the fat tissues was in the form of DDE. In the nursing seals fully 90 percent of the ΣDDT in both fat and blood portions was in the form of DDE. Both *A. callorhini* and *P. fluctus* lice living on 2-month sucklings had 95 percent of the ΣDDT in the DDE form.

In harp seals Jones et al. (*16*) found that DDE was also the major fat-soluble metabolite of DDT. For example, in fat tissue DDE content of mothers and their 8-14-day-old pups was 72 percent and 74 percent, respectively, of the ΣDDT found.

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LITERATURE CITED

(1) *Addison, R. F., S. R. Kerr, J. Dale, and D. E. Sargeant. 1973.* Variation of organochlorine residue levels with age in Gulf of St. Lawrence harp seals (*Pagophilus groenlandicus*). J. Fish. Res. Board Can. 30(5): 596-600.

(2) *Addison, R. F., M. E. Zinck, and R. G. Ackman. 1972.* Residues of organochlorine pesticides and polychlorinated biphenyls in some commercially produced Canadian marine oils. J. Fish. Res. Board Can. 29(4): 349-355.

(3) *Anas, R. E. 1974.* DDT plus PCB's in blubber of harbor seals. Pestic. Monit. J. 8(1): 12-14.

(4) *Anas, R. E., and A. J. Wilson, Jr. 1970.* Organochlorine pesticides in fur seals. Pestic. Monit. J. 3(4): 198-200.

(5) *Anas, R. E., and A. J. Wilson, Jr. 1970.* Organochlorine pesticides in nursing fur seal pups. Pestic. Monit. J. 4(3): 114-116.

(6) *Anas, R. E., and D. D. Worlund. 1975.* Comparison between two methods of subsampling blubber of northern fur seals for total DDT plus PCB's. Pestic. Monit. J. 8(4): 261-262.

(7) *Armour, J. A., and J. A. Burke. 1970.* Method for separating polychlorinated biphenyls from DDT and its analogs. J. Ass. Offic. Anal. Chem. 53(4): 761-768.

(8) *Brewerton, H. V. 1969.* DDT in fats of Antarctic animals. New Zealand J. Sci. 12: 194-199.

(9) *Brown, N. J., and A. W. A. Brown. 1970.* Biological fate of DDT in a sub-Arctic environment. J. Wildl. Manage. 34(4): 929-940.

(10) *Cramer, J. 1973.* Model of the circulation of DDT on Earth. Atmos. Environ. 7: 241-256.

(11) *Eddie, B., W. J. L. Sladen, and K. F. Meyer. 1966.* Serologic studies and isolation of bedsonia agents from northern fur seals on Pribilof Islands. Am. J. Epidemiol. 84(2): 405-410.

(12) *Frank, R., K. Ronald, and H. E. Braun. 1973.* Organochlorine residues in harp seals (*Pagophilus groenlandicus*) caught in eastern Canadian waters. J. Fish. Res. Board Can. 30(8): 1053-1063.

(13) *Gaskin, D. E., R. Frank, M. Holdrinet, K. Ishida, C. J. Walton, and M. Smith. 1973.* Mercury, DDT, and PCB in harbour seals (*Phoca vitulina*) from the Bay of Fundy and Gulf of Maine. J. Fish. Res. Board Can. 30(3): 471-475.

(14) *George, J. L., and D. E. H. Frear. 1966.* Pesticides in the Antarctic. J. Appl. Ecol. 3 (suppl.): 155-167.

(15) *Holden, A. V., and K. Marsden. 1967.* Organochlorine pesticides in seals and porpoises. Nature 216: 1274-1276.

(16) *Jones, D., K. Ronald, D. M. Lavigne, R. Frank, M. Holdrinet, and J. F. Uthe. 1976.* Organochlorine and mercury residues in the harp seal. Sci. Total Environ. 5: 181-195.

(17) *Kim, K. C. 1971.* The sucking lice (*Anoplura: Echinophthiriidae*) of the northern fur seal; descriptions and morphologic adaptation. Ann. Entomol. Soc. Amer. 64(1): 280-292.

(18) *Kim, K. C. 1972.* Louse populations of the northern fur seal (*Callorhinus ursinus*). Am. J. Vet. Res. 33(10): 2027-2036.

(19) *Kim, K. C. 1975.* Ecology and morphological adaptation of the sucking lice on the northern fur seal. Proc. Symp. Biol. Seals, University of Guelph, Canada, 1972. Repp. P.-V. Reun. Conf. Int. Explor. Mer. 169: 504-515.

(20) *Kim, K. C., R. C. Chu, and G. P. Barron. 1974.* Mercury in tissues and lice of northern fur seals. Bull. Environ. Contam. Toxicol. 11(3): 281-284.

(21) *Koeman, J. H., W. H. M. Peters, C. J. Smit, P. S. Tjioe, and J. J. M. DeGoeij. 1972.* Persistent Chemicals in Marine Mammals. TNO Nieuws 27: 570-578.

(22) *Koeman, J. G., and H. van Genderen. 1966.* Some preliminary notes on residues of chlorinated hydrocarbon insecticides in birds and mammals in the Netherlands. J. Appl. Ecol. 3 (suppl.): 99-106.

(23) *Robinson, J., A. Richardson, A. N. Crabtree, J. C. Coulson, and G. R. Potts. 1967.* Organochlorine residues in marine organisms. Nature 214: 1307-1311.

(24) *Shaw, S. B. 1971.* Chlorinated Hydrocarbon Pesticides in California Sea Otters and Harbor Seals. Calif. Fish and Game 57(4): 290-294.

(25) *Sladen, W. J. L., C. M. Menzie, and W. L. Reichel. 1966.* DDT residues in Adelie penguins and a crabeater seal from Antarctica. Nature 210: 670-673.

(26) *U.S. Environmental Protection Agency. 1971.* Analysis of Pesticide Residues in Human and Environmental Studies. Perrine Primate Research Laboratory, Perrine, Fla.

(27) *Woodwell, G. M., P. P. Craig, and H. A. Johnson. 1971.* DDT in the biosphere: where does it go? Science 174: 1101-1107.

Organochlorine Pesticide Residues in Plain Chachalacas from South Texas, 1971-72[1]

Wayne R. Marion [2]

ABSTRACT

Plain chachalacas (Ortalis vetula) *from the intensively cultivated and sprayed Lower Rio Grande Valley of Texas were analyzed for pesticide residues during 1971 and 1972. Residues of eight organochlorine pesticides and a polychlorinated biphenyl were identified in fat tissues of specimens collected from four study areas. Chemicals detected in all 24 birds and average residue levels (±SD) in ppm wet weight were: DDT (1.52±4.12), DDE (2.48±2.09), dieldrin (0.23±0.59), endrin (0.13±0.52), and Aroclor 1248 (0.17±0.20). Residue levels varied considerably, but the majority of the fat tissues contained significantly less than 1 ppm of these chemicals.*

Because birds of this species feed primarily on unsprayed native fruits rather than on sprayed crops, they adsorb very few pesticides through their diet. Although birds from exposed areas near cultivated fields had generally higher residues than had birds from less exposed areas, these herbivores generally had much lower residues than would most birds living near heavily treated lands. During the present study there was no evidence that plain chachalacas died as a direct result of exposure to agricultural chemicals, nor was there evidence that eggshells of this species have thinned significantly since 1900.

Introduction

The Lower Rio Grande Valley of Texas is predominantly a semitropical agricultural region with heavy pesticide use, primarily on cotton (*1*). Within this region, plain chachalacas (*Ortalis vetula*) inhabit small, isolated tracts of dense, brushy woodland (*5*) and feed primarily on small fruits of native plants (*6*). The majority of the chachalacas live close to cultivated fields which are sprayed intensively with agricultural pesticides. Pesticide residue levels in the birds were determined and compared according to the birds' proximity to agricultural activities.

Eggshell thinning in some populations of wild birds has been recognized as a problem associated with environmental contamination by DDE and related chemicals (*9*). To determine whether such a pattern exists in chachalacas, shell thickness of eggs collected during the present study were compared to museum specimens of eggshells collected in South Texas before 1900.

Methods

Fat tissues of 24 birds collected from four study areas in the Lower Rio Grande Valley were analyzed for organochlorine and polychlorinated biphenyl (PCB) residues. Three of the areas, Anzalduas Dam, McManus Farm, and Santa Ana National Wildlife Refuge, are isolated dense brushland in southern Hidalgo County surrounded by fields under intensive cultivation. The Falcon Dam area, a narrow strip of riparian vegetation adjacent to the Rio Grande in western Starr County, was not closely associated with intensive farming.

Of the 24 fat samples analyzed, 10 were from Santa Ana Refuge, 10 from Anzalduas Dam, and 2 each were from McManus Farm and Falcon Dam study areas. For convenience in comparing residue levels, sample collection sites were classified according to proximity and probable exposure to agricultural chemicals. "Central" samples were taken from birds collected more than 400 m from the nearest cultivated fields. Samples from birds collected nearer the adjacent fields were labeled "peripheral." Five samples from central and 5 from peripheral

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locations were analyzed for each of the larger areas, Santa Ana Refuge and Anzalduas Dam. All samples obtained at McManus Farm and Falcon Dam were considered peripheral.

Samples were frozen in 150-ml glass containers and maintained at approximately -18°C. A general pesticide scan for residues of organochlorine pesticides and PCB's was conducted on all fat tissues in laboratories of the Department of Agricultural Analytical Services at Texas A&M University. Analyses were modified slightly from those outlined in Section 211 of a manual by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare (*10*). Each fat sample was thoroughly homogenized in anhydrous sodium sulfate and extracted several times using petroleum ether. A Buchner funnel containing sharkskin filter paper was used to decant supernatant from these extractions into a suction flask. Fat solution was transferred to a tared beaker using small portions of petroleum ether. Petroleum ether was evaporated and the beaker was weighed. Lipid residues were partitioned with acetonitrile saturated with petroleum ether and cleaned with florisil. The cleaned extract was analyzed for pesticide residues by electron-capture gas chromatography with parameters as described by Reynolds (*8*).

Residue levels are reported in parts per million (ppm) on a whole tissue wet-weight basis. Mean residues for all areas were compared using Duncan's new multiple range test (*2*). Mean residues in samples obtained at central and peripheral collection sites were also compared using a t-test (*7*).

Chachalaca eggshells collected during this study were air-dried for several months. Eggshell thickness was determined using a Starrett 1010-m dial gauge calibrated in 0.01-mm units and expressed as the mean of measurements made at three points near the waist of the egg. Chachalaca eggshells collected in southern Texas before 1900 and preserved at the Smithsonian Institution—National Museum of Natural History, Washington, D.C., were similarly measured and the data were statistically compared with those from recent eggshells using a pooled t-test (*7*).

Results and Discussion

Eight organochlorine pesticides including BHC, chlordane, DDT, DDE, dieldrin, endrin, hexachlorobenzene (HCB), and toxaphene were reported in one or more fat samples from collected birds. A polychlorinated biphenyl (PCB), Aroclor 1248, occurred in birds from all collection areas except Anzalduas Dam.

All 24 fat samples contained residues of *p,p'*-DDT and its major metabolite, *p,p'*-DDE. Twenty-one samples contained dieldrin; 12 contained Aroclor 1248. Endrin was found in 8 fat samples, HCB in 3, toxaphene in 2, chlordane in 1, and benzene hexachloride (BHC) in 1.

Mean fat tissue residue levels for 5 major pesticides were generally highest in specimens from Anzalduas, Santa Ana, and McManus Farm, which are closer to agricultural spraying than is Falcon Dam (Table 1). Duncan's new multiple range test revealed no significant differences in residue levels among study areas, except for DDE. Fat in specimens from peripheral areas at Anzalduas Dam and Santa Ana Refuge contained significantly higher mean residues ($P<0.05$) of DDE than did fat from birds at Falcon Dam. The small sample size undoubtedly restricted the power of Duncan's test in detecting these differences.

At Anzalduas and Santa Ana study areas, birds collected in peripheral locations had generally higher residue levels than had those from central locations. Comparisons of these differences yielded nonsignificant t values ($P>0.05$) of 1.03, 1.40, 0.77, 1.19, and 1.06 for Aroclor 1248, DDT, DDE, dieldrin, and endrin, respectively. Once again, the highly variable nature of these residue levels and the relatively small sample size severely restricted

TABLE 1. *Mean residue levels of five pesticides in fat tissues of plain Chachalacas, Lower Rio Grande Valley, Texas—1971-1972.*

Study Area	No. Samples	Mean Pesticide Residues, ppm wet weight				
		Aroclor 1248	*p,p'*-DDT	*p,p'*-DDE	Dieldrin	Endrin
Falcon Dam	2	0.14±0.06 (0.10–0.18)	0.03±0.02 (0.01–0.04)	0.07±0.02 (0.05–0.08)	0.00	0.00
Anzalduas						
Peripheral	5	0.00	5.46±8.49 (0.72–20.53)	1.89±0.79 (0.86–2.86)	0.79±1.22 (0.0–2.86)	0.53±1.13 (0.0–2.55)
Central	5	0.00	0.54±0.51 (0.09–1.35)	0.99±0.79 (0.17–2.12)	0.03±0.03 (0.0–0.04)	0.04±0.07 (0.0–0.16)
Santa Ana						
Peripheral	5	0.42±0.13 (0.24–0.58)	0.69±0.53 (0.19–1.54)	4.25±2.22 (1.78–6.98)	0.08±0.04 (0.04–0.14)	0.02±0.04 (0.0–0.10)
Central	5	0.22±0.24 (0.18–0.49)	0.39±0.16 (0.22–0.64)	3.65±2.65 (1.54–8.17)	0.17±0.19 (0.06–0.50)	0.00
McManus Farm	2	0.28±0.01 (0.27–0.29)	0.50±0.06 (0.46–0.54)	2.77±0.78 (2.21–3.32)	0.05±0.03 (0.03–0.07)	0.00
Mean		0.17±0.20 (0.0–0.58)	1.52±4.12 (0.01–20.53)	2.48±2.09 (0.05–8.17)	0.23±0.59 (0.0–2.86)	0.12±0.52 (0.0–2.55)

the power of this statistical test in detecting these differences. Quantities of pesticides in tissues are generally related to food habits and history of exposure (*3*). Chachalacas which were close to cultivated fields were presumably more heavily exposed to agricultural chemicals than were birds and vegetation some distance from intensive farming; so, too, was their food supply. Although not statistically significant, residue levels in fat of birds from peripheral locations were higher than those from central locations; but overall, these birds had remarkably low pesticide residue levels.

Residue levels in chachalacas were much lower than in ring-necked pheasants (*Phasianus colchicus*) from highly agricultural areas. Pheasants feed in agricultural fields, creating a direct dietary pathway for pesticides to enter their bodies. In rice-growing areas of the Sacramento Valley, California, fat tissues of ring-necked pheasants contained an average of 123 ppm DDT and its metabolites; the maximum level was 5,448 ppm. Mean concentration of dieldrin in fat of these birds was 0.8 ppm (*4*). Even higher levels have been reported for pheasants in California. In 1962, the same investigators reported that fat from four hen pheasants in a treated agricultural area contained 1,236-2,930 ppm DDT, 306-717 ppm DDE, and 0.1-25 ppm dieldrin; considerably lower levels were found in birds from untreated areas (*3*).

Chachalaca eggshells are thicker than those of other gallinaceous birds. Sixty-three eggshells collected in southern Texas before 1900 had a mean thickness of 0.57±0.12 mm; the range was 0.49-0.74 mm. This was slightly higher than the average thickness (0.50±0.06 mm, range 0.41-0.66 mm) of 72 eggshells collected during the present study. The difference in eggshell thickness between pre-pesticide eggs and recent ones was not significant ($t=1.87$, $P>0.05$) and there was little evidence to suggest that pesticides caused this slight difference.

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LITERATURE CITED

(*1*) *Burns, J.E. 1974.* Organochlorine pesticide and polychlorinated biphenyl residues in biopsied human adipose tissue—Texas, 1969-72. Pestic. Monit. J. 7(3/4):122-126.

(*2*) *Duncan, D. B. 1955.* Multiple range and multiple F tests. Biometrics 11(1):1-42.

(*3*) *Dustman, E. H., and L. F. Stickel. 1969.* The occurrence and significance of pesticide residues in wild animals. Ann. New York Acad. Sci. 160(1):162-172.

(*4*) *Keith, J. O., and E. G. Hunt. 1966.* Levels of insecticide residues in fish and wildlife in California. Trans. N. Am. Wildl. Nat. Resour. Conf. 31:150-177.

(*5*) *Marion, W. R. 1974.* Status of the Plain Chachalaca in south Texas. Wilson Bull. 86(3):200-205.

(*6*) *Marion, W. R. 1976.* Plain Chachalaca food habits in south Texas. The Auk 93(2):376-379.

(*7*) *Ostle, B. 1963.* Statistics in Research: Basic Concepts and Techniques for Research Workers. Iowa State Univ. Press, Ames. 583 pp.

(*8*) *Reynolds, L. M. 1969.* Polychlorobiphenyls (PCB's) and their interference with pesticide residue analysis. Bull. Environ. Contam. Toxicol. 4(3):128-143.

(*9*) *Stickel, L. F., and L. J. Rhodes. 1970.* The thin eggshell problem. Pages 31-35 *in* J. W. Gillett, ed. The biological impact of pesticides in the environment. Oregon State Univ. Press, Corvallis. 210 pp.

(*10*) *U.S. Department of Health, Education, and Welfare. Food and Drug Administration. 1972.* Pesticide analytical manual. Vol. I.

Insecticide Residues on Stream Sediments in Ontario, Canada[1]

J. R. W. Miles

ABSTRACT

Insecticide residues on suspended and bottom sediments of streams of Ontario, Canada, have been studied in a tobacco-growing and a vegetable muck area. The proportion of TDE to DDT was <1 in water and >1 in bottom sediments. The ratio of TDE to DDT in bottom material increased linearly from the contamination point at stream source to the mouth of Big Creek in Norfolk County, Ontario. Bed load samples contained three to six times greater concentrations of insecticides than bottom material. Adsorption of insecticides on suspended sediment decreased in order DDT > TDE > dieldrin > diazinon, which is consistent with the water solubility of these compounds.

Introduction

Insecticide analyses of environmental water samples are usually performed on the whole unfiltered sample (*5*). Because the whole water, including sediment, is the environment of fish, crustaceans, and aquatic insects, analysis of the whole-water sample produces data pertinent to biological significance of insecticides. Whole-water analyses combined with water discharge data also are used to calculate transport of insecticides from a stream to the receiving body of water. However, the state of an insecticide, i.e., whether pure particles, adsorbed on sediment, or dissolved in water, can affect biological action because some organisms prefer to feed on sediments (*3*) and because insecticides adsorbed on suspended sediment are eventually deposited and become part of the bottom material (*6*). In the study reported here the author has analyzed insecticide presence in whole-water samples, suspended sediments, bed load, and bottom material of streams in Ontario, Canada.

Methods

Water samples were collected in 1100-ml narrow-neck bottles clamped to an 8-m aluminum pole. Depth integration was achieved by moving the bottle from just below the surface to within 30 cm of the bottom while the bottles were filling with water. Bottles were sealed with tin-foil-lined caps for transport to the laboratory. Contents of two bottles were combined as one sample in a tared 2-liter florence flask (Fig. 1) and the weight of flask plus samples was recorded. Walls of the two sample bottles were rinsed with the same 10-ml acetone which was transferred to the florence flask. A second acetone rinse of 7 ml was also transferred to the flask. A 35-mm magnetic stirring bar was inserted, 50 ml 1:1 hexane/benzene was added, and the flask neck was covered with aluminum foil previously rinsed with hexane. The flask was stirred 15 minutes using enough torque that the vortex pulled the extracting solvent completely into the water. The flask was removed and

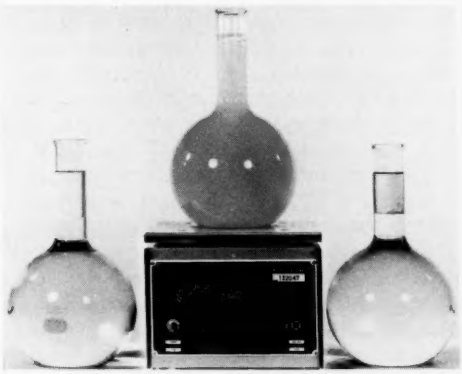

FIGURE 1. *Equipment for extracting insecticide residues from water samples*

[1] Contribution No. 648, Research Institute, Agriculture Canada, University Sub P.O., London, Ontario, Canada N6A 5B7.

left standing 15 minutes. The separated extract layer was transferred to a 250-ml separatory funnel with a Teflon stopcock by a suction tube adapter fitted into the separatory funnel neck. Three extractions were made using fresh hexane/benzene and the three extracts were combined in the separatory funnel. The lower aqueous layer was discarded. The extract was dried by adding 10 g anhydrous sodium sulfate prerinsed with benzene and hexane and poured from the neck of the separatory funnel through a filter funnel containing glass wool which had been rinsed with hexane into a 500-ml round-bottom flask for concentration on a rotary evaporator. Recoveries of insecticides from fortified distilled water were all >90 percent.

SEDIMENT SEPARATION

Water samples for sediment separation were collected at the same time and in the same manner as those for whole-water analysis. The sediment was separated by filtration through a Millipore filter apparatus using 4.25-cm-diameter Whatman GF/C fiber glass papers with nominal porosity of 0.45 μm. Residues were extracted from the filtered sediment with acetone, followed by 1:1 hexane:benzene in a conical flask. Three successive extractions were completed and the combined extracts were dried with anhydrous sodium sulfate before fractionation (*9*). A separate 4-liter sample of water was also taken and filtered through a tared filter paper to obtain the weight of the sediment loading.

Bottom material samples were collected using a sampler designed by the author; it consisted of a steel can, 8.5 cm in diameter and 4.5 cm deep, attached to the end of an 8-m aluminum pole. The can was permitted to settle on the bottom of the stream in inverted position. On rotation of 180° the can sampled a 6-cm-deep portion of bottom material. Five samples of mud were taken from near the bank to mid-stream, and combined into one sample. After the standing water was poured off, the mud was mixed in a pyrex glass tray. Three hundred grams of the mixed sample was placed in a 900-ml narrow-neck glass bottle. One hundred ml of acetone was added and the bottle was swirled to mix. Four hundred ml hexane was added and the bottle was stoppered and tumbled end over end for 1 hour. The supernatant liquid was poured into a 1-liter separatory funnel, the acetone was removed by several distilled water washes, and the hexane extract was dried with anhydrous Na_2SO_4. The moisture content of a 50-g sample of the mud was determined so that results could be reported on a dry-weight basis. Bed load samples were taken with a Bogardi T3 bed load sampler (Fig. 2; *2*). The sampler was lowered from a bridge to the stream bottom and left in position 4 hours. The fluid sample was filtered and extracted as described above for separation of sediment from water samples. Fractionation of extracts on florisil has been described previously (*9,10*).

GAS CHROMATOGRAPHY

Two model 1400 and one model 1200 Varian Aerograph gas chromatographs were used. All columns were 2 m long by 2 mm ID and operated at 180°C. Two 1400 models were equipped with ^3H electron-capture detectors. The column of one model was packed with 5 percent XE60; the other used a liquid phase mixed before coating, 3 percent DC 200/4.5 percent QF-1. The column of the model 1200 was also packed with mixed DC 200/QF-1 but this instrument was equipped with ^3H electron-capture detector in series with Rb_2SO_4 alkali flame ionization detector.

Results and Discussion

BOTTOM MATERIAL

An earlier article (*11*) reported that although in water the ratio of TDE to DDT is <<1, in practically all analyses of bottom mud the ratio is >1. This indicates that the process of dechlorination of *p,p'*-DDT to *p,p'*-TDE was occurring in the bottom material. These findings are consistent with data of Hill and McCarty (*7*) who report that DDT is degraded more readily under anaerobic than aerobic conditions.

If the ratio of TDE to DDT is calculated from the data on bottom mud published earlier (*11*), there is a steady increase in the ratio from spring through summer to fall. For Muskoka River bottom mud from May through September 1971, the TDE:DDT values were 1.6, 1.9, 1.9, 2.4, and 5.4. Since DDT was banned from use in

FIGURE 2. *Bogardi bed load sampler*

Ontario in 1970 the above data could mean that DDT on eroded soil incorporated in the bottom mud in the spring was gradually converted to TDE by microorganism activity from May through September.

Because it requires time for bottom material to move downstream the author sampled a stream for bottom material from source to mouth all in the same day to assess any differences in residue content and ratios. The stream selected was Big Creek in Norfolk County, Ontario, previously described (*10,11*). Big Creek drains a tobacco-growing area; DDT-contaminated soil averaging about 3.5 ppm ΣDDT (*4*) erodes into the upper reaches of the stream. Residues found at the six sampling stations from source to mouth in 1972 are shown in Table 1. Dieldrin concentrations increased gradually from source to mouth but there appears to be no regularity in actual DDT concentration in the bottom material of these six stations. However, there is a regular increase in ratio of *p,p'*-DDE to *p,p'*-DDT and an even more pronounced increase in ratios of *p,p'*-TDE to *p,p'*-DDT from stream source to mouth. Overall change in TDE:DDT from source to mouth is 20 times! The increase in ratio of TDE to DDT can be explained by the longer contact time of adsorbed DDT residues with anaerobic microorganisms as they move from the source down to the mouth, a distance of about 42 km. Since the DDE:DDT ratio also increased steadily from source to mouth one must assume that the bottom material also harbors organisms containing dehydrochlorinase. A repeat of the above experiment at four locations in 1973 revealed the same trend but the range of values was not quite so dramatic: from source to mouth TDE:DDT ratios were 0.2, 0.4, 0.5, and 0.6.

TABLE 1. *Insecticide residues on bottom material at six stations from source to mouth of Big Creek, Ontario—1972*

Sampling Stations	Residues, ppb dry weight		Residue Ratios		
	ΣDDT	Dieldrin	*p,p'*-TDE	*p,p'*-DDE	*p,p'*-DDT
1 Stream source	23.8	<0.3	0.1	0.2	1
2	58.5	0.8	0.2	0.2	1
3	6.9	<0.3	0.8	0.7	1
4	13.0	0.6	1.0	0.9	1
5	26.1	1.3	1.2	1.0	1
6 Stream mouth	34.2	1.4	2.0	1.5	1

BED LOAD

Simultaneous bed load and bottom material samples were taken at monthly intervals from June through October 1973 (Table 2). With one exception, August 14, all residues on bed load samples were much greater than those in the bottom material. In fact, average DDT in the bed load was three times that in the bottom material. Dieldrin was also three times greater and endosulfan was six times greater in the bed load. The bed load is the shifting mass of detritus and sediment which forms the interface between the water and bottom material and provides the environment of benthic organisms. The above data would indicate that animals living in the bed load may be exposed to more insecticide than would be suggested by analysis of bottom material alone. The average ratio of TDE to DDT in bottom material was 1.24; in the bed load the ratio was 0.38. This again indicates that the DDT residues in the bottom material have had a longer period under anaerobic conditions, producing more TDE.

TABLE 2. *Insecticide residues on bed load and bottom material of Big Creek, Norfolk County, Ontario—1973*

Sampling Date	Residues, ppb dry weight					
	DDT		Dieldrin		Endosulfan	
	Bed Load	Bottom Material	Bed Load	Bottom Material	Bed Load	Bottom Material
June 26	198	30	6	1.2	2	<0.1
July 10	45	26	4	1.3	<1	<0.1
Aug. 14	21	27	1	1.7	3	0.7
Sept. 25	100	35	8	1.3	3	0.2
Oct. 2	30	18	2	1.1	1	0.6
Oct. 16	62	18	2	0.7	1	0.2

NOTE: Bed Load = shifting mass of detritus and sediment collected with the Bogardi bed load sampler.
Bottom Material = more permanent bottom mud.

SUSPENDED SEDIMENT

Residues on suspended sediment in Big Creek in 1973 ranged from 8 to 100 percent of the whole-water analyses, as shown in Table 3. Residues in sediment expressed as percent of the whole-water analysis are generally proportional to the sediment load. Although TDE and dieldrin concentrations in water samples were significant, up to 2.0 ng/liter and 2.7 ng/liter, respectively, only traces of TDE and dieldrin were found on the sediment. This is consistent with the solubility of the two chemicals, i.e., 3 times and 13 times that of *p,p'*-DDT (*1*). In some instances, namely, April 10, May 1, 8, 22, and June 12, the percent of ΣDDT on sediment was much less than that of *p,p'*-DDT or *p,p'*-DDE (Table 3). This was because TDE, present in the whole-water sample, contributed to ΣDDT but no TDE was detected on the sediment. The average value for ΣDDT expressed as ppm dry weight of sediment is 0.11 ppm. This value is 4.2 times the average ppm in the bottom material samples from Big Creek during the same sampling period. Since DDT residues in the bottom material are only one-fourth those on the sediment one must conclude that considerable dilution with uncontaminated bottom material occurs upon deposit of sediment and/or the DDT degrades more quickly in the bottom material.

Comparable data on residues in sediment as percent of whole-water analyses for three streams in the Holland Marsh, which contains organic soil used for vegetable production, are shown in Table 4. Concentrations in water and mud of this region are much greater than those of Big Creek, as demonstrated by the greater quantities of insecticides on the sediment. These are

TABLE 3. *Insecticide residues on suspended sediment of Big Creek, Ontario—1973*

Sampling Date	Sediment Load, γG/liter	Residues[1]							
		∑DDT		*p,p'*-DDT		*p,p'*-DDE		Dieldrin	
		%	ppm	%	ppm	%	ppm	%	ppm
March 27	0.0600	68	0.07	68	0.05	67	0.02	16	<0.01
April 3	0.0825	81	0.19	72	0.11	97	0.04	29	0.01
10	0.0543	63	0.08	89	0.06	97	0.02	ND	ND
17	0.0430	90	0.13	100	0.07	76	0.13	ND	ND
24	0.0364	45	0.10	40	0.06	88	0.04	ND	ND
May 1	0.0440	70	0.10	85	0.05	83	0.05	ND	ND
8	0.0222	51	0.13	85	0.08	48	0.05	ND	ND
15	0.0222	33	0.07	36	0.04	60	0.03	ND	ND
22	0.0082	29	0.15	33	0.09	63	0.06	ND	ND
June 12	0.0330	64	0.09	90	0.05	100	0.04	ND	ND
July 17	0.0082	8	0.06	19	0.06	ND	ND	17	0.04
Sept. 12	0.0182	53	0.17	32	0.05	ND	ND	ND	ND
Oct. 9	0.0116	42	0.10	69	0.10	ND	ND	ND	ND

NOTE: ND = none detected.
TDE was present in whole-water analyses from trace to 2 ng/liter but only traces were detected on suspended sediments.
Dieldrin after April 3 was present in whole water from 0.7 to 2.7 ng/liter but only traces were detected on suspended sediment, except July 17.
[1]Residues expressed as percent of whole-water analysis and as ppm on dry weight of sediment.

TABLE 4. *Insecticide residues on suspended sediment of streams in Holland Marsh, Ontario—1973*

Sampling Date	Sediment Load, γG/liter	Residues[1]											
		∑DDT		*p,p'*-DDT		*o,p'*-DDT		*p,p'*-DDE		*p,p'*-TDE		Dieldrin	
		%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Stream A													
Mar. 22	0.0044	38	13.4	36	8.6	42	2.3	47	1.8	39	0.7	8	0.5
29	0.0076	75	12.9	79	9.8	72	1.8	73	0.9	40	0.3	13	0.5
Apr. 5	0.0083	89	14.0	90	10.3	96	2.1	75	0.9	77	0.7	42	0.5
12	0.0026	35	11.5	38	8.7	30	1.2	41	0.9	19	0.8	5	0.5
Stream B													
Mar. 29	0.0028	44	17.9	43	12.4	45	2.4	43	1.3	57	1.9	8	0.6
Apr. 5	0.0068	47	8.9	48	6.0	49	1.4	46	0.8	42	0.7	11	0.4
12	0.0040	32	4.7	35	3.2	30	0.6	37	0.5	18	0.4	3	0.2
Stream C													
Mar. 22	0.0148	88	1.5	86	1.0	96	0.2	90	0.1	91	0.3	18	0.1
29	0.0247	85	0.9	96	0.6	93	0.1	78	0.1	57	0.1	10	<0.1
Apr. 5	0.0203	79	1.3	86	0.9	95	0.2	67	0.1	35	0.1	9	<0.1
12	0.0142	65	1.2	70	0.8	90	0.1	60	0.1	46	0.2	13	0.1
AVERAGE		62		64		67		60		47		13	

[1]Residues expressed as percent of whole-water analysis and as ppm on dry weight of sediment.

much greater than the residues found in the bottom material which contained *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-TDE in parts per billion range. This agrees with the above discussion of data from the Big Creek study. The percentages of insecticides on the sediment are again roughly proportional to the sediment load. It is significant that *p,p'*-DDT, *o,p'*-DDT, and *p,p'*-DDE were all >60 percent adsorbed on the sediment, but the more water soluble *p,p'*-TDE averaged 47 percent adsorption and dieldrin averaged 13 percent, ranging from 9 to 42 percent. These ranges may appear wide but this was not a controlled laboratory sediment experiment; composition of sediments could vary between sampling dates, greatly affecting adsorption. Since both sediments and insecticides determined in stream samples are allochthonous, great variability can be expected.

Diazinon was present in all whole-water samples (≤80 ng/liter) but was not detected on any suspended sediment samples. It is soluble to 40 ppm (*12*) in water and evidently remains in solution rather than adsorbing onto the sediments. Four samples reported in Table 4, all from stream A, contained parathion in the whole-water samples ranging from 13 to 19 ng/liter, but no parathion was detected in the sediments. Parathion has a water solubility of 24 ppm (*12*) so presumably it would also be in solution and not adsorbed to the sediment. Ethion, which has a solubility of 0.6 ppm in water as determined by this laboratory, was present in three whole-water samples in quantities as high as 33 ng/liter. No ethion was detected in the filtered sediment.

This author has observed that some laboratories studying environmental water samples have analyzed only the filtered water. Since plant and animal life are exposed to the whole water including sediment (*3,8*), such an approach is unrealistic. The study of stream sediments reported herein has been performed in considerable

detail, including separation of sediment-borne insecticide residues from the whole-water samples and separate analyses of suspended sediment, bed load, and bottom material. The study demonstrates that concentrations of insecticide residues on stream sediments vary with the type of sediment and its location in the stream. Even residues of the supposedly recalcitrant DDT are in a state of change, with the ratios of metabolites DDE and TDE varying in proportion to the parent DDT on the different sediments and on the same sediment at different locations upstream or downstream.

Acknowledgments

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LITERATURE CITED

(1) *Biggar, J. W., and R. L. Riggs. 1974.* Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia 42(10):383-391.

(2) *Bogardi, J. 1942.* Vizfolyasok hordalekmerese [Sediment measurements on watercourses]. Hidrologiai Kozlony 7-12. Budapest.

(3) *Coker, R. E. 1954.* Streams, Lakes and Ponds. Harper and Row, New York, p. 139.

(4) *Harris, C. R., and W. W. Sans. 1971.* Insecticide residues in soils on 16 farms in southwestern Ontario—1964, 1966, and 1969. Pestic. Monit. J. 5(3):259-267.

(5) *Hartung, R. 1975.* Accumulation of chemicals in the hydrosphere. Page 189 *in* R. Haque and V. H. Freed, ed. Environmental Dynamics of Pesticides. Plenum Press, N.Y.

(6) *Hassett, J. P., and G. F. Lee. 1975.* Pesticides in the aqueous environment. Page 180 *in* R. Haque and V. H. Freed, ed. Environmental Dynamics of Pesticides. Plenum Press, N.Y.

(7) *Hill, D. W., and P. L. McCarty. 1967.* Anaerobic degradation of selected chlorinated hydrocarbon pesticides. J. Water Pollut. Control Fed. 39(8):1259-1277.

(8) *Jones, J. R. E. 1964.* Fish and River Pollution. Butterworths, London, p. 5.

(9) *Miles, J. R. W. 1972.* Conversion of DDT and its metabolites to dichlorobenzophenones for analysis in the presence of polychlorinated biphenyls. J. Ass. Offic. Anal. Chem. 55(5):1039-1041.

(10) *Miles, J. R. W., and C. R. Harris. 1971.* Insecticide residues in a stream and a controlled drainage system in agricultural areas of southwestern Ontario, 1970. Pestic. Monit. J. 5(3):289-294.

(11) *Miles, J. R. W., and C. R. Harris. 1973.* Organochlorine insecticide residues in streams draining agricultural, urban-agricultural, and resort areas in Ontario, Canada—1971. Pestic. Monit. J. 6(4):363-368.

(12) *Spencer, E. Y. 1973.* Guide to the Chemicals Used in Crop Protection. Pub. No. 1093 6th ed. Research Branch, Agriculture Canada, Ottawa. 542 pp.

Chronology of Organochlorine Compounds in Lake Michigan Fish, 1929-66

William J. Neidermyer and Joseph J. Hickey [1]

ABSTRACT

Museum specimens of six species of Lake Michigan fish collected from 1929 through 1966 were analyzed for dieldrin, polychlorinated biphenyls (PCB's), and DDT analogs. Dieldrin first appeared in the 1955 specimens. Residues were low and exhibited no trend with time. PCB's and DDT analogs appeared in 1949 in the same samples. Both PCB's and ΣDDT increased progressively through 1965. PCB residues showed no decreasing trend. ΣDDT peaked in 1965. PCB's and DDE were always detected together. The ratio of PCB to DDT showed no trend from 1949 to 1966.

Introduction

Insecticide residues in Great Lakes fish have been monitored since 1965 by the Great Lakes Fishery Laboratory of the Fish and Wildlife Service, U.S. Department of Interior (*8*). Lake Michigan fish contain the highest concentrations of organochlorine insecticides of all Great Lakes fish. The high residue levels are in part the result of the widespread usage of these compounds in the watershed and the disproportionately brief flushing period and low biomass density of Lake Michigan, according to Veith (*9*). Veith has established baseline concentrations of DDT and polychlorinated biphenyls (PCB's) in Lake Michigan fish in 1971. The present report presents an historical profile of chlorinated hydrocarbon residues in Lake Michigan fish from 1929 to 1966. Historical residue levels of DDT analogs and PCB's have been reported for a marine fish species (*6*), marine sediments (*4*) , and membranes of peregrine falcon (*Falco peregrinus*) eggshells (*7*) in other ecosystems.

Sampling Procedures

Specimens were obtained from the Museums of Zoology at the University of Michigan and at the University of Wisconsin in Madison. At the time of acquisition the specimens were preserved in glass jars filled with ethyl alcohol. Some specimens had been preserved originally in formalin before being transferred to ethyl alcohol by the museum staff. Authors obtained whole fish when available. From large fish a sample of the epaxial muscle was analyzed. All samples were placed in glass jars with aluminum-foil-lined caps and were frozen until analysis. The following common and scientific names of the six species of fish examined are from the list published by the American Fisheries Society (*2*): emerald shiner (*Notropis atherinoides*), fourhorn sculpin (*Myoxocephalus quadricornis*), rainbow smelt (*Osmerus mordax*), kiyi (*Coregonus kiyi*), bloater (*Coregonus hoyi*), and alewife (*Alosa pseudoharengus*).

Analytical Methods

The WARF Institute, Inc., in Madison, Wis., used gas chromatography to analyze all samples for dieldrin, PCB's, DDT, TDE, and DDT. Large samples were homogenized with the aid of a Hobart food chopper. Small samples were snipped finely with tissue scissors. A portion of the sample was weighed into a 150-ml beaker. The sample was ground with about 30 g anhydrous sodium sulfate and dried 48-72 hours. The sample was placed in a 33-by-94-mm Whatman extraction thimble and extracted for 8 hours on a Soxhlet extractor with 70 ml ethyl ether and 170 ml petroleum ether. The solvent was reduced to near dryness on the steam bath and placed in a 40°C oven for 4 hours. The beaker was removed from the oven, contents were desiccated, weighed, and the amount of lipid in the sample was calculated.

An aliquot of the sample was cleaned on a standardized florisil column. Typical elutions were 150 ml 5 percent ethyl ether in petroleum ether, followed by 240 ml 15 percent ethyl ether in petroleum ether. After florisil cleanup the resulting solutions were concentrated on a 5-10-ml steam bath and made to 25 ml with hexane.

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The first elutions from the florisil were injected on a gas chromatograph to determine the approximate amount of PCB interference. An aliquot of this solution ≤5 μg DDE and 20 μg PCB was run through a silicic acid / celite column according to the Armour-Burke method for separating PCB's from DDT and its analogs (*1*). Each resulting solution was chromatographed and the amounts of the various pesticides were determined. A Barber-Colman model 5400 gas chromatograph with a 4-ft-by-3-mm glass column packed with 5 percent DC-200 on 80/100-mesh Gas-Chrom Q was used for the gas chromatography. The carrier gas, nitrogen, was maintained at 80 ml/min; the injector, column, and detector temperatures were 215°, 200°, and 245°C, respectively.

Recovery rates of PCB (Aroclor 1254), dieldrin, DDE, TDE, and DDT were 60-80, 65-95, 86-96, 80-90, and 75-95 percent, respectively. The detection limit for dieldrin and DDT analogs was 0.01 ppm; for PCB's, 0.1 ppm. No confirmatory tests were performed.

Results and Discussion

Because the years of storage in formalin and ethyl alcohol had dehydrated fish tissues, residues are expressed on a lipid basis (Table 1). Gibbs et al. reported that formalin, ethyl alcohol, and isopropyl alcohol affected the concentrations of heavy metals in specimens of myctophid fish (*3*). MacGregor (*6*) reported that formalin had no effect on the residues of DDT and its metabolites and PCB's in specimens of myctophid fish preserved from 1949 to 1972. Authors do not know whether formalin and ethyl alcohol affected the specimens used in this study. Reinert (*8*) has shown that lipid content, size of fish, and season of capture may affect considerably the concentration of chlorinated hydrocarbons observed in tissue. Although such effects were not controlled in the present analyses, authors believe that the data represent the magnitude of the residue levels present at time of analysis.

Dieldrin first appeared in two samples from 1955. No trends in residue levels of dieldrin during subsequent years could be determined. Levels were usually low, ranging from 0.20 to 2.39 ppm (Table 1).

Commercial manufacture of PCB's began in the United States in 1929 (*5*). No PCB's were detected in museum samples until 1949, when the kiyi had 5.17 ppm and the alewife had 4.85 ppm (Table 1). Hom et al. found that the deposit of PCB's in marine sediments from the Santa Barbara basin began about 1945 (*4*). They associated this finding with the rapid increase in PCB use during World War II as electrical-insulating fluids and paint additives, and in a variety of miscellaneous applications which release these compounds into the environment. Presumably Lake Michigan began receiving PCB deposits about the same time, although a critical gap in Lake Michigan data from 1943 to 1948 prevents an absolute statement to this effect.

Levels of PCB's in Lake Michigan fish show a progressive increase from 1949 through 1966. Hom et al. (*4*) found a similar increase through 1967 in marine sediments. MacGregor (*6*) found no trend with time in the concentrations of PCB's in a myctophid fish off southern California between 1949 and 1966. Veith (*9*) established baseline concentrations for 1971 in Lake Michigan fish of 70.80 ppm and 30.00 ppm PCB's (lipid basis) in alewife and bloater, respectively. These concentrations are

TABLE 1. *Concentrations of organochlorines in Lake Michigan fish, 1929-66*

Species[1]	Year	Percent Lipid[2]	Residues, ppm lipid weight					PCB: ΣDDT Ratio
			Dieldrin	PCB	DDE	TDE	DDT	
Emerald shiner	1938	0.26	ND	ND	ND	ND	ND	
Fourhorn sculpin	1936	1.69	ND	ND	ND	ND	ND	
	1949	0.11	ND	ND	ND	ND	ND	
	1951	3.66	ND	3.40	8.54	5.19	5.66	0.18
	1955	7.02	0.20	4.39	9.31	13.70	5.48	0.15
	1965	1.20	ND	24.88	37.32	43.54	6.22	0.29
	1966	2.17	ND	17.43	38.02	0.83	34.25	0.24
Rainbow smelt	1931	0.35	ND	ND	ND	ND	ND	
	1942	0.35	ND	ND	ND	ND	ND	
	1942	0.54	ND	ND	ND	ND	ND	
	1960	0.34	ND	59.31	11.86	ND	ND	5.00
	1966	10.03	0.55	12.34	30.91	14.09	11.91	0.22
Kiyi	1949	4.88	ND	5.17	7.31	3.24	3.03	0.38
Bloater	1929	0.18	ND	ND	ND	ND	ND	
	1961	3.87	1.09	7.85	4.96	2.31	2.18	0.83
	1965	12.03	0.93	43.96	34.67	29.96	2.89	0.65
	1966	14.24	1.34	39.36	38.03	22.44	4.61	0.60
Alewife	1949	23.95	ND	4.85	2.18	1.68	ND	1.26
	1951	24.65	ND	1.02	4.14	3.71	ND	0.13
	1952	27.76	ND	3.50	6.98	1.64	2.62	0.31
	1953	31.27	ND	5.78	6.57	2.54	0.53	0.60
	1954	20.39	ND	1.85	6.34	4.07	ND	0.18
	1955	10.57	2.39	5.37	13.98	12.12	3.72	0.18
	1965	0.13	ND	79.69	25.81	13.07	19.36	1.37

NOTE: ND = not detected.
[1]Scientific names of species sampled: emerald shiner, *Notropis atherinoides*; fourhorn sculpin, *Myoxocephalus quadricornis*; rainbow smelt, *Osmerus mordax*; kiyi, *Coregonus kiyi*; bloater, *Coregonus hoyi*; alewife, *Alosa pseudoharengus*.
[2]Results expressed on liquid basis because prolonged storage of museum specimens in formalin and ethyl alcohol dehydrated fish tissues.

slightly lower than the values found in the present study: 79.69 ppm in alewife in 1965, and 39.36 ppm in bloater in 1966 (Table 1). Reinert reported increasing levels of PCB's in Lake Michigan coho salmon (*Oncorhynchus kisutch*) and lake trout (*Salvelinus namaycush*) from 1972 through 1974, and stable levels in bloaters during the same time period (R. E. Reinert, Great Lakes Fishery Laboratory, U.S. Department of Interior, 1975: personal communication). Thus it appears that the concentrations of PCB's in Lake Michigan fish remain high despite the restriction of sales to closed system users in 1971 by Monsanto Company, St. Louis, Mo., the sole producer of PCB's in the United States.

Among museum specimens, PCB's were never detected in the absence of DDE. The ratio of PCB's to ΣDDT should be important in reflecting the trend of concentrations of these compounds. Data from the present study show no trend from 1949 through 1966. Values range from 0.13 to 5.00 (Table 1).

DDT and its analogs were first detected in 1949. They appeared in the same specimens in which PCB's were first detected: kiyi, 13.58 ppm; alewife, 3.86 ppm (Table 1), and progressively increased to 1965. Hom et al. (*4*) reported that DDE in marine sediments deposited off the California coast progressively increased from about 1952 through 1967; MacGregor (6) reported increasing DDT metabolites in California myctophid fish from 1949 through 1970; and Peakall (*7*) reported DDE in the membranes of peregrine falcon eggshells at least as early as 1948. These four independent studies agree in their determination of the time that DDT and its metabolites began accumulating in the environment. That date corresponds closely with the increase in the manufacture and use of DDT during and immediately after World War II. However, the critical years of 1946 and 1947 are not represented in the samples of these four studies. Establishing the presence of DDE in these two years is important to the phenomenon of eggshell thinning attributed to the presence of DDE (5).

Data for alewives and bloaters (Figure 1) indicate that the concentration of ΣDDT in Lake Michigan fish peaked in 1965. These data and results from the Great Lakes Fishery Laboratory suggest that residues have been decreasing since the late 1960's. R. E. Reinert reports a continued decrease of ΣDDT through 1974 in Lake Michigan bloaters, coho salmon, and lake trout (personal communication: see previous allusion).

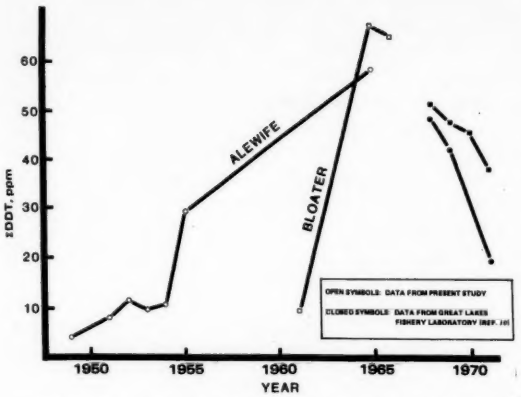

FIGURE 1. *Trend of ∑DDT concentrations in Lake Michigan alewives and bloaters, 1949-71.*

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LITERATURE CITED

(*1*) *Armour, J. A., and J. A. Burke. 1970.* Method for separating polychlorinated biphenyls from DDT and its analogs. J. Ass. Offic. Anal. Chem. 53(4):761-768.

(*2*) *Bailey, R. M., J. E. Fitch, E. S. Herald, E. A. Lachner, C. C. Lindsey, C. R. Robins, and W. B. Scott. 1970.* A list of common and scientific names of fishes from the United States and Canada. 3rd ed. Amer. Fish. Soc. Spec. Publ. 6. Ann Arbor, Mich. 150 pp.

(*3*) *Gibbs, R. H. Jr., E. Jarosewich, and H. L. Windom. 1974.* Heavy metal concentrations in museum fish specimens: effects of preservatives and time. (Science 184 (4135):475-477.

(*4*) *Hom, W., R. W. Risebrough, A. Soutar, and D. R. Young. 1974.* Deposition of DDE and polychlorinated biphenyls in dated sediments of the Santa Barbara basin. Science 184(4142):1197-1199.

(*5*) *Hubbard, H. L. 1964.* Chlorinated biphenyl and related compounds. *In* R. E. Kirk and D. F. Othern, eds. Encyclopedia of Chemical Technology 5:289. Second rev. ed.

(*6*) *MacGregor, J. S. 1974.* Changes in the amount and proportions of DDT and its metabolites, DDE and DDD, in the marine environment off southern California, 1949-72. Fishery Bull. 72(2):275-293.

(*7*) *Peakall, D. B. 1974.* DDE: its presence in peregrine eggs in 1948. Science 183(4125):673-674.

(*8*) *Reinert, R. E. 1970.* Pesticide concentrations in Great Lakes fish. Pestic. Monit. J. 3(4):233-240.

(9) *Veith, G. P. 1975.* Baseline concentrations of polychlorinated biphenyls and DDT in Lake Michigan fish, 1971. Pestic. Monit. J. 9(1):21-29.

(10) *Tait, H. D. 1972.* Progress in Sport Fishery Research 1971. Great Lakes Fishery Laboratory, U.S. Department of Interior, pp. 86-120.

Preliminary Study of the Occurrence and Distribution of DDT Residues in the Jordan Watershed, 1971[1]

Jacob D. Paz[2]

ABSTRACT

Data obtained from the Jordan watershed in 1971 revealed the presence of DDT and its metabolites at various levels along the food chain. Detectable levels of ΣDDT in water of the Jordan River and two fish ponds ranged from 0.019 to 0.500 ppb, which is 1/10 to 1/500 the maximum level permitted in water by the U.S. Government. Mean residue in phytoplankton was 0.906 μg/g; in zooplankton the mean was 6.49 μg/g. ΣDDT residue in fish of the Jordan watershed averaged 0.37 mg/kg in carp, 2.59 mg/kg in benith, and 3.34 mg/kg in sardines.

Introduction

This study investigated the presence of DDT residues in the Jordan watershed. No previous studies have been conducted on DDT and its residues in that body of water.

The area of the Jordan watershed is 2,730 km². Its major components are the Jordan River and its tributaries: the Dan, the Snir, and the Hermon Rivers. The water level is sustained by spring and effluent discharges as well as by runoff.

Most of the 100,000 inhabitants of the watershed live in villages and towns, where they are employed in agriculture and industry.

The watershed discharges $9 \cdot 10^{8}$ m³ of water annually into the Sea of Galilee (Lake Kinneret). This includes approximately $1.4 \cdot 10^{7}$ m³ of domestic sewerage effluent, $5.4 \cdot 10^{7}$ m³ of fish pond effluent, and $1.4 \cdot 10^{7}$ m³ drainage from agricultural fields (7).

Most of the effluents flow directly into the Sea of Galilee. The Hula Valley in northern Israel, which was once a swamp, is also drained by the Jordan River. This valley is intensely cultivated and has received extensive applications of DDT and other pesticides. Runoff and wind are mechanisms by which various pesticide residues likely find their way to the Jordan River.

Sampling

Samples were collected at the three sites labeled in Figure 1: two fish ponds in Dafna, northern Israel, near the source of the Dan River; the Huri bridge at the southern end of the Hula Valley; and a spot 500 feet from the tip of the Jordan River before it enters the Sea of Galilee.

SITE 1

Surface water samples were collected at the edge of each pond and 30 feet within the ponds. Subsamples were placed in 1-liter polyethylene bottles.

Phytoplankton was collected with No. 63 mesh nets and refrigerated in 1-liter bottles. Carp (*Cyprinus carpio*) were caught in nets within 25 feet of the ponds' edges.

SITES 2 AND 3

Water samples were collected at the edge of the river and midriver. Presumably the current provided good mixing. One liter of water consisting of three subsamples was placed in a bottle.

Phytoplankton was collected midriver and at the edge of the river with No. 63 mesh nets, and refrigerated in bottles.

Zooplankton was caught midriver and at the bank with No. 230 mesh nets. Samples were refrigerated in 1-liter bottles.

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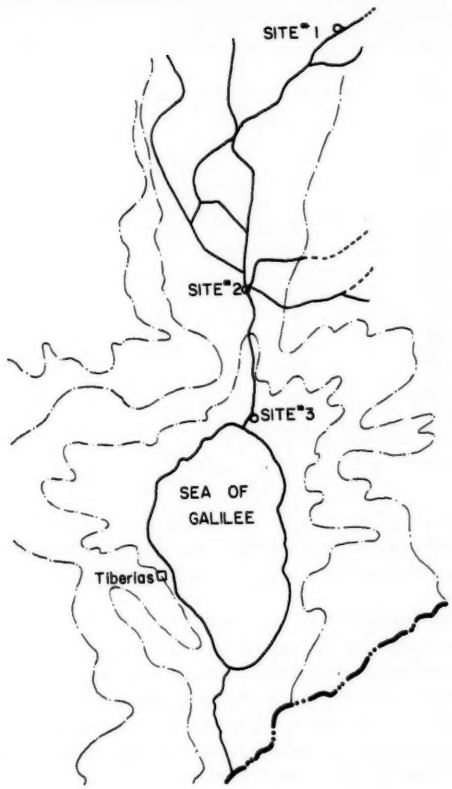

FIGURE 1. *Sites in Jordan watershed sampled for DDT residue, 1971*

Benith (*Barbus longiceps*) and sardines (*Acanthobrama terrae-sanctae*) which inhabit the Jordan River were caught by the net and refrigerated at 4°C.

Analytical Procedures

EXTRACTION

Water—One liter of water was filtered through Whatman No. 4 filter paper. Samples were extracted with hexane as described in *Standard Methods for Examination of Water and Wastewater* (*8*).

Phytoplankton—The sample was filtered through fiber glass cloth and ground mechanically. Extraction was carried out with acetonitrile and the sample was re-extracted with 10 ml hexane. The concentration of phytoplankton was determined on a dry-weight basis (*4*).

Zooplankton—The sample was filtered through Whatman No. 4 filter paper, dried under silica gel, and weighed. Zooplankton was ground mechanically. Extraction was carried out with 10 ml hexane. The sample was filtered and stored for further cleanup.

Fish—The extraction procedure followed the Extraction of Lean Tissue with Hexane recommended in the *Guide to the Analysis of Pesticide Residues* (*9*).

Ten to twenty g tissue from the midbellies of fish was placed in a homogenizer with 10 g sand-washed acid and anhydrous Na_2SO_4. This was ground to a fine powder. The sample was extracted with 50 ml hexane in a 250-ml beaker on a steam bath of 50°C and subsequently vacuum-filtered. The sample was re-extracted three times with 20 ml hexane and transferred to 100 ml in a volumetric flask. The volume was adjusted to 100 ml with hexane to compensate for loss from evaporation. The volumetric flask with its contents was placed at 4°C for 1 hour to precipitate the bulk of the fat. For further cleanup 25 ml of extract was taken (*2*).

CLEANUP

Liquid partition was followed as described by de Faubert Maunder et al (*2*).

To remove traces of fatty acids which could interfere with gas chromatography, an activated alumina column was used (*1*). Alumina was heated for 1 hour at 450°C and cooled in a desiccator. Ten percent water was added. Ten g activated alumina anhydrous hexane was transferred to a chromatographic column in the form of a slurry, which was allowed to settle. A 5-cm layer of anhydrous sodium sulfate was added. The hexane extract was poured completely through and washed three times with 90 ml hexane. The eluate was concentrated to the desired volume by evaporation in a water bath (*6*).

QUANTITATIVE ANALYSIS

A model 1200 Varian Aerograph gas chromatograph (GC) with an electron-capture detector and an all-glass column was used for pesticide quantification. Operating conditions were:

Column	8 feet long, 1 mm by 3 mm
Column Packing	3 percent QF-1 as a liquid support on solid support Varaport No. 39
Carrier Gas	N_2
Initial Pressure	60 psi
Gas Flow	30 ml/min

Column Temperature	180°C
Detector Temperature	225°C

Residues were reported as ΣDDT (DDT+DDE+TDE). Concentration of DDT was determined by a series of standards injected into the GC. Means of the peaks were plotted against the concentration of DDT. No attempts were made to isolate and identify another peak that appeared on the GC.

Retention times for the various pesticides were, in minutes: DDE, 4.2; *p,p'*-DDT, 4.4; TDE, 5.2; *o,p'*-DDT, 5.5.

Results

WATER

Table 1 shows pesticide concentrations of DDT residues in water of Dafna fish ponds and the Jordan River at various locations. Quantities ranged from $^1/_{10}$ to $^1/_{500}$ the level permitted by the U.S. Government in a water supply (*10*).

PHYTOPLANKTON

Concentrations of ΣDDT residue in phytoplankton varied from 0.1 to 3.7 μg/g dry weight (Table 2). ΣDDT residues in the Daphna fish ponds were much lower than in the Jordan River, perhaps because DDT runoff from agricultural uses finds its way to the river.

TABLE 1. *DDT concentrations in water of Jordan River and Daphna fishponds, Israel—1971*

Sample	Residues, ppb		
	DDE	DDT	ΣDDT
Pond 10			
1			ND
2	0.032		0.032
3			ND
Pond 11			
4	0.038		0.038
5	0.02		0.02
6	0.073		0.073
7	0.02		0.02
Mean			0.026
Jordan River			
8	0.019		0.019
9	0.500		0.500
10		0.024	0.024
11		0.02	0.02
12			ND
13			ND
Mean			0.08
14	0.032	0.04	0.076
15	0.09		0.090
16	0.02		0.020
17			ND
18			ND
19			ND
20	0.04		0.040
Mean			0.032

NOTE: See map, Figure 1, for sampling sites.
ND = not detected (<0.2 ppb).
No significant differences observed among Daphna fish ponds and locations along Jordan River from which samples were taken.

TABLE 2. *DDT concentrations in pyhtoplankton of Jordan watershed, Israel—1971*

Sample	Residues, μg/g dry weight		
	DDE	*p,p'*-DDT	ΣDDT
Pond 10			
20			ND
21			ND
22			ND
Pond 11			
23	0.3		0.3
24	0.25		0.25
25	0.15		0.15
Jordan River			
26	0.19	0.23	0.42
27	0.3	0.16	0.46
28	0.75	0.27	1.02
29	0.75	1.25	2.00
30	3.00	0.79	3.79
31	1.10	1.20	2.30
32	0.40	0.80	1.20
33	0.70	0.90	1.60
34	0.53		0.53
35	0.09	0.4	0.49
Mean [1]			0.906

NOTE: See map, Figure 1, for sampling sites.
ND = not detected (<0.2 ppb).
[1] SD of mean = 0.906±1.05.

ZOOPLANKTON

In zooplankton samples from the Jordan River ΣDDT concentrations varied from 3.4 to 17.0 μg/g in the forms of DDE and *p,p'*-DDT (Table 3). High concentration of ΣDDT may be due to difference in metabolism of DDT and absorption directly from water, and from zooplankton's feeding on phytoplankton.

FISH

As indicated in Table 4, carp from fish pond 10 which had been spawned April 1971 weighed 30-50 g. ΣDDT residue ranged from 0.18 to 0.82 mg/kg. Carp from pond

TABLE 3. *DDT concentrations in zooplankton of Jordan watershed, Israel—1971*

Sample	Residues, μG/G dry weight			
	DDE	*p,p'*-DDT	TDE	ΣDDT
50	4.8	0.41		5.21
51	2.0	1.4		3.4
52	16.0	1.0		17.0
53	1.7	1.7		3.4
54	4.0	3.2		7.2
55				ND
56	7.2			7.2
57				ND
58	12.5			12.5
59		3.7	1.2	4.9
60	3.2	5.6		8.8
61	2.0	5.0		7.0
Mean[1]				6.49

NOTE: See map, Figure 1, for sampling site.
ND = not detected (<0.1 μg/g).
[1] SD of mean = 6.49±4.64.

TABLE 4. *DDT concentrations in carp from Israeli ponds, 1971*

Sample	Weight, g	Residues, mg/kg wet weight				
		DDT	*p,p'*-DDT	*o,p'*-DDT	TDE	Σ DDT
Pond 11						
100	860					ND
101	1,010	0.14			0.7	0.34
102	300					ND
103	300					ND
104	400	0.25				0.25
105	950					ND
106	700	3.9			0.46	4.36
Pond 10						
107	51					0.18
108	52				0.47	0.47
109	40	0.05			0.44	0.49
110	45					ND
111	32					ND
112	30					ND
113	31	0.1	0.2	0.1		0.4
114	45					lost
115	51	0.1				0.2
116	50	0.16	0.66		0.1	0.82
117	51	0.18				0.18
Mean[1]						0.37

NOTE: See map, Figure 1, for sampling sites.
ND = not detected (<0.01 mg/kg).
[1] SD of mean = 0.37±0.21.

11 had been spawned April 1970 and weighed 300-1,000 g. ΣDDT residue ranged from 0.25 to 4.36 mg/kg.

Benith from the Jordan River (Table 5) weighed between 150 and 1,035 g. ΣDDT residue ranged from 0.1 to 8.78 mg/kg. Sardines from the river (Table 6) ranged from 12 to 108 g. ΣDDT residue ranged from 0.1 to 16.6 mg/kg.

The high DDT residues in benith and sardines might be attributed to the fact that both fish are at the top of the food chain; ΣDDT increases along the chain. DDT concentration increased with age and weight of the fish

TABLE 5. *DDT concentrations in benith of Jordan River, Israel—1971*

Sample	Weight, g	Residues, mg/kg wet weight				
		DDT	*p,p'*-DDT	*o,p'*-DDT	TDE	ΣDDT
119						
120	150	0.1				0.1
121	260	0.5	0.9		1.3	2.6
122	190					ND
123	190	0.7				ND
124	160	0.9				ND
125	270	3.0	0.31			1.81
126	403	1.17	0.9			1.8
127	1,035	0.25	2.57			8.78
128	470	8.8	1.76			4.24
129	254		2.0		0.6	2.95
130	163	1.42	1.0		0.6	2.4
131	430	0.60				ND
132	380	1.0	3.53			4.95
136	396	0.3	0.32		0.10	1.42
138	163					1.70
139	150		0.7			1.50
144	210		1.81			1.81
Mean[1]						2.59

NOTE: ND = not detected (<0.01 mg/kg).
[1] SD of mean = 2.59±2.56.

TABLE 6. *DDT concentrations in sardines of Jordan River, Israel—1971*

Sample	Weight, g	Residues, mg/kg wet weight				
		DDE	*p,p'*-DDT	*o,p'*-DDT	TDE	ΣDDT
145	12		0.1			0.1
146	85		2.77	3.0	3.05	8.82
147	15			1.18	0.9	2.09
148	15					ND
149	49	4.8	2.8	7.0	2.0	16.6
150	40	0.1	1.6			1.7
154	14	0.3	0.1	0.3	0.4	1.1
156	79	1.2	0.9	0.9		3.0
160	108	1.33	1.61	0.11	0.1	3.16
161	97	0.62	2.81	3.12		6.55
162	76	2.55	1.77	0.2	0.1	4.62
163	84	3.6	1.1	0.3	1.52	6.26
164	42	0.1	0.96	0.1	0.4	1.56
Mean[1]						3.34

NOTE: ND = not detected (<0.01 mg/kg).
[1] SD of mean = 3.34±2.54.

(Figure 2). Based on scale studies, highest concentration ranges occurred in fish 3-5 years old.

Discussion

Primary evidence demonstrates that DDT residue in the lentic environment of the Jordan watershed has been absorbed into the food chain and has increased from one trophic level to the next. Thus a mechanism based upon absorption and solubility difference regulates concentration levels in various components of the lentic environment. The partition coefficient for DDT between water and fish was $4.6 \cdot 10^4$. The partition coefficient is as follows: the ratio uptake of DDT occurs from one trophic level to the next. Partition coefficients can be shown in the following ratios (concentrations are expressed as the mean values):

$$\frac{\text{DDT concentration in phytoplankton}}{\text{DDT concentration in water}} = 1.4 \cdot 10$$

$$\frac{\text{zooplankton}}{\text{phytoplankton}} = 9.5$$

$$\frac{\text{fish}}{\text{zooplankton}} = 2.2 \cdot 10^2$$

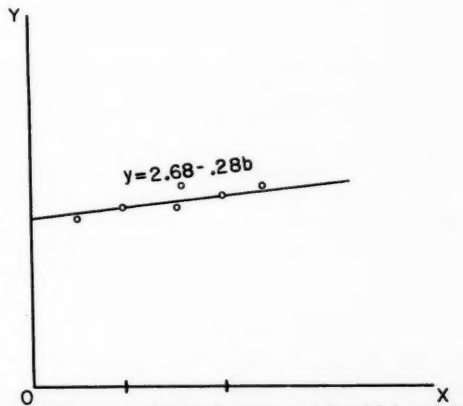

FIGURE 2. *Correlations between weight of fish and DDT residue in Jordan watershed, 1971*

Various degrees of partition coefficients have been published. Hamelink (*4*) reported partition coefficients of $1.0 \cdot 10^{4}$ between water and fish. Gunther (*3*) reported various coefficients: 10^{3}, 10^{4}, 10^{5}, 10^{6}, 10^{7}. These partition coefficients depend upon such factors as the amount of DDT in each trophic level, and metabolism and temperature.

Sources of DDT in the Jordan watershed are agricultural uses in the Hula and the upper Galilee Valleys. Pesticides are transported to the Jordan River by wind and runoff from rain. The Jordan watershed discharges annually $9 \cdot 10^{9}$ m^{3} water into the Sea of Galilee, which supplies a third of Israel's water. It is quite feasible that DDT finds its way to the lake. Although the amount of ΣDDT residue in this study does not exceed the 42 ppb deemed acceptable by the United Nations World Health Organization, Lahav (*5*) reported that TDE and *o,p'*-DDT in the Sea of Galilee exceed the WHO permissible level by a factor of 100.

DDT and its metabolites were concentrated in fish tissues at various levels. Differences in feeding habits and age may explain the variation in residue levels among the three species within a body of water.

Mean ΣDDT residue was 0.37 ppm in carp, 2.59 ppm in benith, and 3.34 ppm in sardines. Residues found in the tissues included DDT and its metabolites DDE, TDE, *p,p'*-DDT, and *o,p'*-DDT. The level of 5 mg/kg DDT permitted by WHO was exceeded in sardines by a factor as large as three.

These data obtained in the summer of 1971 show that agricultural contamination of the Jordan watershed warrants concern for fish, fish-consuming populations, and the affected environment. Further study should be conducted to investigate the full impact of DDT and other pesticides on the Jordan watershed.

LITERATURE CITED

(*1*) *Beynon, K. Y., and K. E. Elgar. 1966.* The analysis for residues of chlorinated insecticides and pesticides. Analyst 91(1080):143-175.

(*2*) *de Faubert Maunder, M. J., H. Egan, E. W. Godly, E. W. Hammond, J. Roburn, and J. Thomson. 1964.* Clean-up of animal fats and dairy products for the analysis of chlorinated pesticide residues. Analyst 89(1056):168-174.

(*3*) *Gunther, F. A., W. E. Westlake, and P. S. Jaglan. 1968.* Reported solubilities of 738 pesticide chemicals in water. Residue Rev. 20:1-148.

(*4*) *Hamelink, J. L., R. C. Waybrant, and R. C. Ball. 1971.* Proposal: exchange equilibriums control the degree chlorinated hydrocarbons are biologically magnified in lentic environments. Trans. Am. Fish. Soc. 100(2):207-214.

(*5*) *Lahav, N., and Y. Kahanovitch. 1974.* Occurrence of pesticides in selected water sources in Israel. Environ. Sci. Technol. 8:762-765.

(*6*) *Pionke, H. B., J. G. Konrad, G. Chesters, and D. E. Armstrong. 1968.* Extraction of organochlorine and organophosphate insecticides from lake waters. Analyst 93 (107):363-367.

(*7*) *Shuval, H. T. 1970.* Developments in Water Analysis Research. Ann Arbor Press. 7 pp.

(*8*) *Standard Methods for Examination of Water and Wastewater. 1971.* Chlorinated hydrocarbon pesticides. Amer. Public Health Assoc., 13th ed., pp. 100-107.

(*9*) *U.S. Department of Health, Education, and Welfare. 1965.* Extraction of lean tissue with hexane. Guide to Analysis of Pesticide Residues, Vol. 1, Sec. II (A.5.a).

(*10*) *U.S. Department of Interior. 1968.* Water Quality Criteria—Report of the National Technical Advisory Committee to the Secretary of the Interior. Federal Water Pollution Control Administration. 233 pp.

Occurrence of Pesticide Residues in Four Streams Draining Different Land-Use Areas in Pennsylvania, 1969-71[1]

John F. Truhlar[2] and Lloyd A. Reed[2]

ABSTRACT

Samples of water, streambed material, fish, and soil were collected in four small drainage basins in Pennsylvania in 1969-71 and analyzed to determine the concentrations of chlorinated hydrocarbon insecticides. Water samples were also analyzed for phenoxy-acid herbicides. Each basin studied represents a predominant land use: forest, general farms, residential areas, and orchards.

All water and fish samples showed pesticide concentrations less than the maximum level recommended by the Public Health Service, U.S. Department of Health, Education, and Welfare. However, no fish were found in the orchard stream.

DDT or one of its metabolites was the most frequently occurring insecticide and was detected in all media sampled except the forest soil. The highest combined concentration of DDT and its metabolites in storm-runoff samples was 11.4 μg/liter in a sample collected from the residential area stream, but the median was higher (0.12 μg/liter) in the orchard than in the residential area (0.02 μg/liter).

A sample of the top 0.5 inch (13 mm) of orchard soil contained 40,000 μg/kg DDT and its metabolites, even though DDT had not been used in the orchards for several years prior to this study. Maximum concentrations detected in other orchard media are 330 μg/kg in streambed material and 3.45 μg/kg in storm runoff.

Dieldrin was the second most frequently occurring insecticide. Other insecticides detected were chlordane, heptachlor epoxide, lindane, and a trace of aldrin in one fish sample. Each stream contained at least one of the following herbicides: 2,4-D, silvex, or 2,4,5-T.

Introduction

This study was conducted to determine the degree of pesticide contamination in four small drainage basins and to determine whether pesticide residues were present in amounts that could be hazardous to humans or to aquatic life. Each basin was chosen to represent a single land use: forest, general farms, residential area, or orchards.

The four basins were selected according to the percentage of drainage area in the desired land-use category and the ease of collecting data during storms. Areas selected are shown in Figure 1. The areas are (1) a 46.2 mi² (119.7 km²) forested area situated in northern Clinton, eastern Potter, and western Lycoming Counties drained by Young Womans Creek; (2) a 15.0 mi² (38.8 km²) general farming area in western Perry County drained by Bixler Run; (3) a 1.85 mi² (4.79 km²) residential area in Dauphin County drained by an unnamed tributary of Spring Creek; (4) a 1.26 mi² (3.26 km²) orchard area in Adams County drained by an unnamed tributary of Latimore Creek.

Samples of streambed material and water were collected periodically from each of the four areas from February 1969 to April 1971 and analyzed for chlorinated hydrocarbon insecticides. Water samples were analyzed for phenoxy-acid herbicides. Insecticide concentrations in local soils and fish, except in the orchard area, were determined once in each area. Data were collected also on streamflow, suspended sediment concentration, and water chemistry.

Sampling and Analysis

Most soil samples were collected from the top 3 inches (76 mm) from different locations in each of the areas and composited into single samples for analysis. Soil samples from the orchard area were divided into three categories:

[1] Originally printed in cooperation with the Pennsylvania Department of Environmental Resources, State Conservation Commission, as Water Resources Investigations 6-75, U.S. Geological Survey, Harrisburg, Pa.

[2] U.S. Geological Survey, Box 1107, Harrisburg, Pa. 17108. Reprints available from this address.

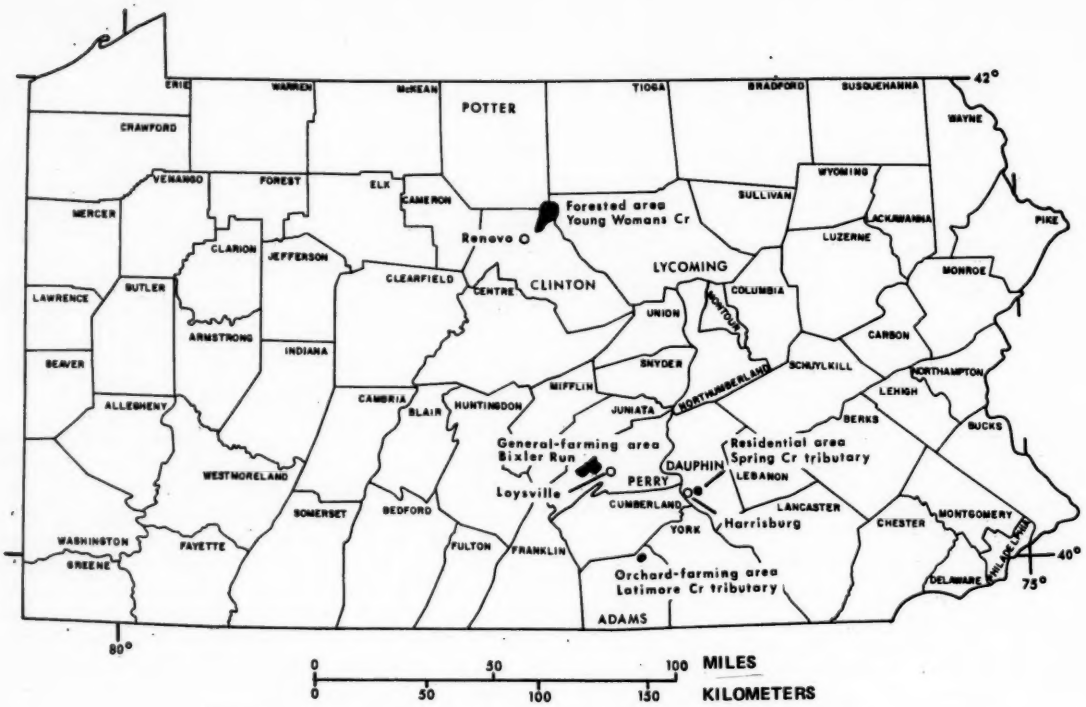

FIGURE 1. *Locations in Pennsylvania sampled for pesticide residues, 1969-71*

the area in open fields and woods, the top 0.5 inch (13 mm) of orchard soil, and the orchard soil 0.5 to 3 inches (13 to 76 mm) deep. Samples were collected from the top 2 inches (51 mm) of the streambed where fine material had been deposited. Samples were collected from different locations in the channel and composited into a single sample for analysis.

Water samples were collected both during base flow periods when streams were normally clear, and during storms when streams were highly turbid. Suspended sediment samples were collected using standard depth-integrating sediment samplers (*6*), and samples for pesticide analyses were collected by wading and sampling, with a container of teflon or glass, throughout the vertical section. Samples for pesticide and suspended sediment concentration were collected simultaneously. Analyses were run on each individual water sample; no composites were made. Pesticide analyses were performed on the whole water sample, including suspended sediment.

Fish samples were collected and separated according to species and age, and frozen. Analyses were performed on the whole fish.

Streamflow data were collected using the existing gauging station records for Young Womans Creek and Bixler Run and by using staff gauges and storm hydrograph recorders installed during the study on the tributaries of Spring and Latimore Creeks.

The basic analytical procedures utilized in the pesticide analyses, and the pesticides which can be detected by these methods, have been described by Goerlitz and Brown (*4*). A list of the pesticides that were detected is shown below. Subsequent tables show only those pesticides that were detected in each medium. Polychlorinated biphenyls (PCB's) were separated from the chlorinated hydrocarbon insecticides by the scheme described by Goerlitz and Law (*5*). The reported values are not corrected for recovery. Mass spectrometry was used for residue confirmation.

Description of Study Areas

FOREST

Nearly 100 percent of the forested area, which is drained by Young Womans Creek, is State forest lands which have light duty roads, hunting camps, and lodges. Water,

chemical, and sediment discharge data have been collected since December 1964 at the Young Womans Creek gauging station near Renovo as part of the Geological Survey hydrologic benchmark station network.

No known pesticide has been applied directly to this forest. The nearest large-scale pesticide application was in 1965 when a part of the Kettle Creek basin north of the Young Womans Creek basin was aerially sprayed with DDT at the rate of 0.5 lb/a. (0.5 kg/ha.) to control fall cankerworm.

GENERAL FARMS

The general farming area, which is drained by Bixler Run, supports dairy farms typical of those located in the valley and ridge sections of the State. Nearly all the crops grown, primarily corn, oats, mixed hay, and alfalfa, are fed to dairy cattle. Water, chemical, and sediment discharge records have been collected since 1954 at the Bixler Run gauging station near Loysville.

Pesticides are used especially to control weeds in corn and insects in alfalfa; application rates and quantities were not determined for the study.

RESIDENTIAL AREA

The residential area is in Dauphin County east of Harrisburg. The land is used primarily for suburban housing in 0.25- to 1-acre (0.1-0.4 ha.) lots. Pesticides are used to control insects and diseases on trees and shrubbery, and to control weeds, undesirable grasses, and insects in lawns. Application rates vary greatly from house to house and year to year. A random survey of homeowners in this area indicated that herbicides, usually applied with a fertilizer, are used more frequently than are insecticides.

Spring Creek tributary which drains this area occasionally received domestic sewage during storms. This sewage, in addition to overland runoff during storms, may be a source of some pesticide residues found in the stream. Pesticides enter the sewers when homeowners wash their spraying equipment or dispose of pesticides directly into sewers.

ORCHARDS

Orchards occupy nearly 70 percent of the area drained by Latimore Creek tributary at the sampling location. Apples are the major crop, but cherries and peaches are also grown.

Pesticide applications for most apples begin in April and continue almost daily, covering the entire orchard area in about a 1-week period. Spraying is discontinued 2-3 weeks before harvest in September or October. Pesticides are applied mainly to control insects and fungus; however, small quantities are used to control rodents and limit the growth of grass and weeds. Most spraying is done by the individual farmer using tractor-towed orchard sprayers equipped with fans to propel the pesticide mist to the interior areas of the trees. Dieldrin and endrin were the only chlorinated hydrocarbon insecticides applied during the period studied here. Exact records of the pesticides used in previous years are not available; however, the operator of the orchards has not used DDT for several years.

Occurrence of Pesticides

DDT or one of its metabolites was found in all areas and in each medium sampled except for soil in the forested area. Dieldrin was the second most commonly detected insecticide. Figure 2 shows where and in which media insecticides were detected.

One or more of the herbicides 2,4,-D, silvex, or 2,4,5-T was detected at least once in each stream. Herbicides in soil, bed material, or fish samples were not analyzed.

SOILS

Results of insecticide analyses of composited soil samples are shown in Table 1. Highest insecticide concentrations were detected in soils from the orchard area. Samples were separated into three composite groups as previously described because higher concentrations were anticipated in this area than in the others. The combined concentration of DDT and its metabolites in the top 0.5 inch (13 mm) of orchard soil was 40,000 μg/kg. The calculated concentration of DDT and its metabolites in the top 3 inches (76 mm) of orchard soil was 14,000 μg/kg, and corresponding values for the residential and general farming soils were 55 μg/kg and 1.7 μg/kg, respectively. No insecticide residues were found in forest soil samples.

The fact that high concentrations of DDT and its metabolites were found in the top 0.5 inch (13 mm) of

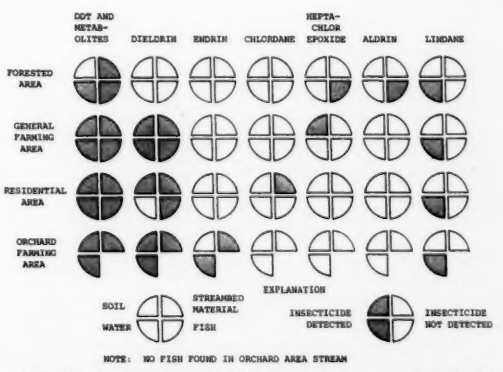

FIGURE 2. *Occurrence of insecticides in soil, streambeds, water, and fish samples from four different land-use areas, Pennsylvania—1969-71*

TABLE 1. *Insecticide residues in soil samples from stream basins draining four different land-use areas, Pennsylvania—1969-71*

Collection Date	Sample Depth	Residues, µg/kg				
		TDE	DDE	DDT	Dieldrin	Heptachlor epoxide
		Forests				
10-15-70	Top 3 inches (76 mm)	0.0	0.0	0.0	0.0	0.0
		General Farms				
5-1-69	Top 3 inches (76 mm)	0.0	1.7	0.0	24	0.6
		Residential Area				
2-27-69	Top 3 inches (76 mm)	4.0	0.0	51	1.7	0.0
		Orchards				
2-27-69	Top 0.5 inch (13 mm)	6,200	6,300	28,000	6,100	0.0
2-27-69	0.5 to 3 inches (13 to 76 mm)	690	1,900	6,200	3,600	0.0
2-27-69	Top 3 inches (76 mm) in adjacent open fields and woods	21	17	77	8.8	0.0

TABLE 2. *Insecticide residues in streambed samples from four different land-use areas, Pennsylvania—1969-71*

Collection Date	Residues, µg/kg					
	Chlordane	TDE	DDE	DDT	Dieldrin	Endrin
			Forests			
6-10-68	0	0.5	0.1	0.5	0.0	0.0
11-27-68	0	0.5	0.0	0.5	0.0	0.0
5-20-69	0	0.0	0.6	0.0	0.0	0.0
7-10-69	0	0.0	0.0	0.0	0.0	0.0
10- 2-69	0	0.2	0.0	0.0	0.0	0.0
11-18-70	0	0.0	0.0	0.0	0.0	0.0
4-15-71	0	0.8	0.9	0.5	0.0	0.0
Mean	0	0.3	0.2	0.2	0.0	0.0
Median	0	0.2	0.0	0.0	0.0	0.0
			General Farms			
2-27-69	0	0.0	0.0	0.0	0.5	0.0
7- 9-69	0	0.0	0.0	0.0	0.0	0.0
10-15-70	0	0.0	0.0	0.0	0.0	0.0
4-13-71	0	0.4	0.5	0.5	0.3	0.0
Mean	0	0.1	0.1	0.1	0.2	0.0
Median	0	0.0	0.0	0.0	0.0	0.0
			Residential Area			
4-30-69	0	7.4	6.9	9.1	0.0	0.0
7- 8-69	0	1.1	1.0	1.5	0.0	0.0
8-28-69	0	1.0	0.0	2.5	TR	0.0
10-15-70	0	47	10	5,900	0.0	0.0
4-13-71	250	5.2	11	5.7	0.2	0.0
Mean	50	12	5.8	1,200	0.0	0.0
Median	0	5.2	6.9	5.7	0.0	0.0
			Orchards			
2-27-69	0	59	30	53	0.0	0.0
4-30-69	0	37	23	50	10	0.0
7- 8-69	0	19	14	31	0.0	0.0
10-15-70	0	190	41	54	7.7	55
4-13-71	0	230	60	37	10	120
Mean	0	110	34	45	5.7	35
Median	0	59	30	50	7.7	0.0

NOTE: TR = trace.

orchard soil even though DDT has not been used for several years, indicates that residues of this insecticide remain primarily in the uppermost soil layers, which contain organic material and clay-size soil particles.

STREAMBEDS

Samples were collected on at least four occasions from streambeds and analyzed for insecticides (Table 2). Ranges observed in the concentration of DDT and its metabolites from each of the four basins are shown in Figure 3. Lowest concentrations were observed in the streams draining the forest and farming areas, and highest concentrations were observed in the streams draining the residential and orchard areas. The sample collected from a residential area near Spring Creek tributary October 15, 1970, had 5,900 μg/kg DDT. This could reflect a slug discharge which passed through the sewer system during a recent storm. Separate sanitary and storm sewers were installed within the residential area during the study period but were not finished until after the study. Prior to completion of the separate sewer system, residential sewage was flushed by direct runoff through storm sewers into Spring Creek tributary.

One streambed sample typical of those analyzed was collected at each area for size analysis. Particle size distributions of these samples are shown below. No sample contained material larger than sand although the materials in all except the residential area streambed are predominantly cobble-sized.

	Sand, %	Silt, %	Clay, %
Forest	63	24	13
General farm	73	12	15
Residential area ..	53	28	19
Orchards	63	24	13

WATER

More than 80 water samples were analyzed for pesticide concentrations (Table 3). Twenty percent were collected during base flow periods when sediment concentrations were low; the remainder were collected during storms when sediment concentrations were high. It was anticipated that pesticide residues observed during storm runoff would be higher than during base flow due to the increased suspension of sediment and organic detritus with which pesticides are associated.

Very low pesticide concentrations were observed in the four base flow and six storm-runoff samples collected from Young Womans Creek. Pesticides were detected in only one base flow and one storm-runoff sample. Bixler Run, like Young Womans Creek, showed very low

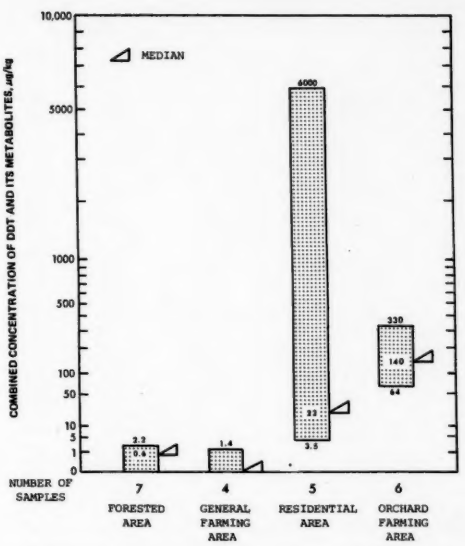

FIGURE 3. *Range in concentration of DDT and its metabolites in streambed samples collected from streams draining four different land-use areas, Pennsylvania - 1969-71*

concentrations. Pesticides were detected in only one of four base flow samples and in seven of ten storm-runoff samples.

Spring Creek tributary was sampled 3 times during base flow and 23 times during storms. Pesticides were not detected in any of the base flow samples. However, nearly all the storm-runoff samples contained pesticide residues. The highest observed concentration of a single pesticide residue in any water sample was the 11.0 μg/liter of DDT found in a storm-runoff sample collected at this sampling site in June 1970.

Latimore Creek tributary was sampled 6 times during base flow and 27 times during storms. Pesticides were detected in three of the base-flow and in all but two of the storm-runoff samples. The highest observed concentration of a single pesticide detected at this sampling site was the 2.50 μg/liter of DDT found in a storm-runoff sample collected May 9, 1969.

The maximum, minimum, and median concentrations of DDT and its metabolites observed in the water samples from each of the four streams are illustrated in Figure 4. The lowest concentrations were observed in the forest and farms; the highest concentrations were observed in the residential area and the orchard. The combined concentration of 11.4 μg/liter of DDT and its metabolites observed in Spring Creek tributary on June 3, 1970, may

TABLE 3. *Pesticide residues in streams draining four different land-use areas, Pennsylvania—1969-71*

Collection Date	Collection Time	Instantaneous discharge, cfs[1]	Sediment concentration, mg/liter	Residues, µg/liter								
				TDE	DDE	DDT	Dieldrin	Endrin	Lindane	2,4-D	Silvex	2,4,5-T
Young Womans Creek (forest)												
2-27-69	—	20	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4- 5-69	1200	171	15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4- 5-69	1730	285	88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4- 5-69	1935	340	108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4- 5-69	2,200	351	65	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01
4- 6-69	0705	392	25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7-10-69	1315	10	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8-14-69	1730	10	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10- 2-69	—	4	BF	0.00	0.01	0.02	0.00	0.00	0.01	0.00	0.00	0.00
11-18-70	1200	288	—	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Base flow	Mean			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Median			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Storm runoff	Mean			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Median			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bixler Run (general farms)												
2-27-69	1045	6.9	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4- 5-69	1545	20	20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4- 5-69	2100	76	48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
5- 1-69	1430	8.0	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5- 9-69	1230	32	—	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
7- 9-69	1200	2.9	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7-23-69	0650	104	900	0.00	0.00	0.00	0.00	0.00	0.00	TR	0.00	0.30
7-23-69	0825	71	399	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07
7-23-69	1440	123	277	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
8-27-69	1315	2.5	BF	0.00	0.00	0.13	0.00	0.00	0.00	—	—	—
7-10-70	1135	96	37	0.08	0.05	0.14	0.08	0.00	0.02	0.00	0.00	0.00
2-22-71	1210	341	838	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
2-22-71	1640	427	342	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
2-22-71	1910	328	307	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Base flow	Mean			0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
	Median			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Storm runoff	Mean			0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.04
	Median			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spring Creek Tributary (residential area)												
4-10-69	1755	11	2,000	0.02	0.00	0.08	0.00	0.00	0.00	0.36	0.04	0.04
4-10-69	1908	4.1	550	0.02	0.00	0.03	0.00	0.00	0.00	0.20	0.00	0.03
4-30-69	1550	0.4	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/ 9/69	0838	36	1,220	0.01	0.00	0.06	0.00	0.00	0.00	0.91	0.05	0.25
6/ 2/69	2205	1.5	205	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/ 2/69	2255	13	760	0.03	0.00	0.20	0.00	0.00	0.00	0.00	0.00	0.00
6/ 2/69	2340	19	1,030	0.02	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00
7/ 8/69	1815	0.3	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7-23-69	0600	115	—	—	—	—	—	—	—	0.00	0.00	0.00
7-23-69	1235	25	98	—	—	—	—	—	—	0.00	0.00	TR
8-28-69	—	0.4	BF	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
9- 8-69	1410	13	600	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
9- 8-69	1500	14	860	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10- 2-69	1545	12	660	0.00	0.00	0.07	0.00	0.00	0.02	—	—	—
10- 2-69	1608	24	446	0.17	0.00	0.18	0.00	0.00	0.00	—	—	—
10- 2-69	1628	41	2,470	0.00	TR	0.12	0.00	0.00	0.02	—	—	—
10- 2-69	1645	36	1,526	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
4- 2-70	0545	78	300	0.00	0.00	TR	0.00	0.00	0.01	—	—	—
6- 3-70	2025	47	2,970	0.36	0.09	11.0	0.00	0.00	0.34	—	—	—
7- 2-70	1000	3.4	32	0.00	0.00	0.01	0.00	0.00	TR	—	—	—
7- 9-70	1445	13	275	0.01	0.01	0.08	0.00	0.00	0.01	0.00	0.00	0.00
9-27-70	1045	25	536	0.00	0.00	0.02	0.00	0.00	0.00	0.01	0.02	0.02
12-17-70	0055	10	221	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-22-71	0915	7.2	44	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00
2-22-71	1420	25	332	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
2-22-71	1755	14	90	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
Base flow	Mean			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Median			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Storm runoff	Mean			0.03	0.00	0.57	0.00	0.00	0.02	0.10	0.01	0.02
	Median			0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00

(*Continued next page*)

TABLE 3 (cont'd.). *Pesticide residues in streams draining four different land-use areas, Pennsylvania—1969-71*

Collection Date	Collection Time	Instantaneous discharge, cfs	Sediment concentration, mg/liter	Residues, µg/liter								
				TDE	DDE	DDT	Dieldrin	Endrin	Lindane	2,4-D	Silvex	2,4,5-T
Latimore Creek Tributary (orchards)												
2-27-69	1530	0.8	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-10-69	1740	2.4	166	0.09	0.08	0.23	0.00	0.00	0.00	0.00	0.00	0.00
4-10-69	1840	1.9	58	0.03	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
4-30-69	1230	0.8	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5- 9-69	0720	3.1	2,670	0.05	0.02	0.08	0.00	0.00	0.00	0.03	0.00	0.00
5- 9-69	0750	3.1	1,450	0.55	0.28	0.64	0.00	0.00	0.00	0.06	0.00	0.01
5- 9-69	0810	4.0	1,660	0.58	0.30	2.50	0.00	0.00	0.00	0.05	0.00	0.00
5- 9-69	0855	2.9	325	0.14	0.09	0.07	0.00	0.00	0.00	0.02	0.00	0.00
5-20-69	1410	0.8	BF	0.04	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00
6- 2-69	2050	0.4	62	0.02	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00
6- 2-69	2110	1.2	390	0.04	0.04	0.07	0.00	0.00	0.00	0.00	0.00	0.00
6-16-69	1030	0.8	BF	0.04	0.01	0.03	0.05	0.00	0.00	0.00	0.00	0.00
7- 8-69	1300	0.3	BF	0.04	0.01	0.01	0.04	0.00	0.00	0.00	0.00	0.00
7-12-69	1545	2.4	872	0.67	0.71	2.07	0.33	0.00	0.00	0.00	0.00	0.00
7-12-69	1600	2.1	523	0.50	0.50	1.45	0.14	0.00	0.00	0.00	0.00	0.00
7-12-69	1700	1.9	119	0.13	0.09	0.23	0.09	0.00	0.00	0.00	0.00	0.00
8-28-69	1115	0.7	BF	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
9- 7-69	2140	4.4	140	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
9- 7-69	2205	4.4	179	0.00	0.00	0.00	0.01	0.00	0.00	—	—	—
10- 2-69	1500	4.4	107	0.00	0.00	0.15	0.00	0.00	0.00	—	—	—
10- 2-69	1600	14	1,310	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
10- 2-69	1920	7.2	41	0.00	0.00	0.12	0.00	0.00	0.00	—	—	—
4- 2-70	1210	39	482	0.30	0.11	0.30	0.00	0.00	0.01	—	—	—
6- 3-70	2135	17	624	0.60	0.21	0.51	0.16	0.00	0.00	—	—	—
7- 2-70	0905	2.7	4	0.06	0.02	0.03	TR	0.00	0.00	—	—	—
7-10-70	1000	11	57	0.00	0.00	0.01	0.00	0.00	0.00	0.08	0.00	0.00
9-27-70	1145	2.9	87	0.04	0.01	0.01	0.00	0.00	0.00	0.02	0.00	0.00
12-16-70	2300	5.3	210	0.02	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00
12-16-70	2345	6.1	315	0.04	0.00	0.00	0.00	0.08	0.00	0.01	0.00	0.00
12-17-70	0225	15	431	0.06	0.00	0.00	0.00	0.15	0.00	0.01	0.00	0.00
12-17-70	0310	14	296	0.07	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00
2-22-71	1015	13	701	0.07	0.05	0.12	0.00	0.00	0.00	0.00	0.00	0.00
2-22-71	1520	11	161	0.01	0.03	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Base flow	Mean			0.02	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.00
	Median			0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Storm runoff	Mean			0.15	0.10	0.32	0.03	0.02	0.00	0.01	0.00	0.00
	Median			0.05	0.03	0.07	0.00	0.00	0.00	0.00	0.00	0.00

NOTE: BF = base-flow sample.
TR = trace.
— = no analysis performed.
[1] To convert cfs to m^3 multiply by 0.02832.

have resulted from a slug discharge. Subsequent samples show approximately the same concentrations observed previously.

None of the pesticide residues detected in the water samples exceeded the maximum permissible concentration (Table 4) recommended by the Public Health Service (*7*). The highest combined concentration of DDT and its metabolites detected in water samples was 11.4 µg/liter, or 27 percent of the maximum permissible concentration. This level was found in a sample collected from Spring Creek tributary on June 3, 1970. The highest combined concentration in Latimore Creek tributary was 3.45 µg/liter, or 8 percent of the maximum permissible concentration, in a sample collected July 12, 1969.

Endrin was detected at a concentration of 0.19 µg/liter, or 19 percent of the maximum permissible concentration, in a water sample collected in Latimore Creek tributary on December 17, 1970. No other pesticides were detected in excess of 2 percent of the recommended maximum permissible concentration for pesticides in public water supplies.

FISH

Fish were collected in March 1970 from three of the four streams investigated. No fish could be found during this sampling period in Latimore Creek tributary, although fish had been observed the previous fall. The fish were separated by species and age, except for the blacknose dace (*Rhinichthys atratulus*, Table 5), and analyzed for insecticides.

Only one compound, DDE, was found in each of the fish samples. It was observed in approximately equal concentrations in the same species of fish from Young Womans Creek and Bixler Run, and in concentrations approximately 10 times greater in the same species from Spring Creek tributary. The highest concentration of DDT and its metabolites in fish samples was 590 µg/kg, or about 12 percent of the recommended maximum (5,000 µg/kg in the edible portion) for food fish (Public

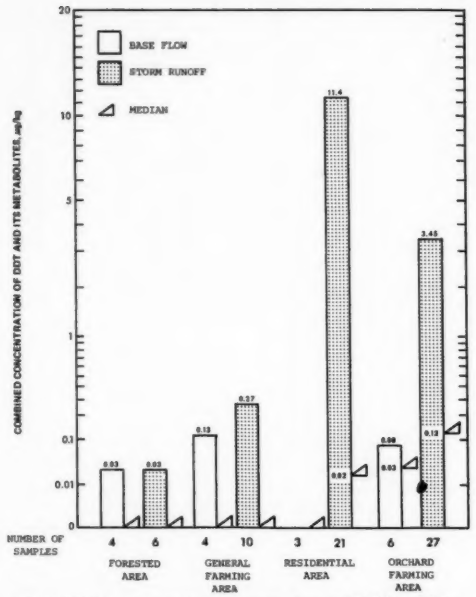

FIGURE 4. *Range in concentration of DDT and its metabolites in streams draining four different land-use areas, Pennsylvania - 1969-71*

Health Service, U.S. Department of Health, Education, and Welfare, 1974: written communication).

Relation of Pesticides to Suspended Sediment

Correlation between suspended sediment concentration and the combined concentration of DDT and its metabolites was examined for each site. No correlation was apparent for either Young Womans Creek or Bixler Run, where only very low concentrations of pesticides were found. The general relationship, showing low pesticide concentrations at base flow and high concentrations only when suspended sediment concentrations were relatively high, was apparent for Spring Creek tributary, but considerable scatter was observed. A fair correlation was found for Latimore Creek tributary, where combined concentration of DDT and its metabolites ranged from 0 to 3.45 µg/liter, with a corresponding range in suspended sediment concentrations of 50 mg/liter to more than 2,000 mg/liter. Figure 5 shows this correlation. DDT is no longer used in the orchards so its only source is the soil; therefore, input to the stream should reflect storm intensity, erosion, and sediment transport.

Particle size distribution was analyzed in five suspended sediment samples from Latimore Creek tributary that were collected simultaneously with samples analyzed for

TABLE 4. *Maximum pesticide concentrations recommended in drinking water supplies, Public Health Service* [1]

Pesticide	Maximum concentration, µg/liter [2]
Endrin	1
Aldrin	17
Dieldrin	17
Lindane	56
Toxaphene	5
Heptachlor	18
Heptachlor epoxide	18
DDT	42
Chlordane	3
Methoxychlor	35
Total organophosphorus and carbamate compounds [3]	100
2-4-5-TP	Individual limits = 100 µg/liter. Sum of any combination of chlorinated phenoxy alkyl pesticides = 100 µg/liter.
2,4,5-T	
2,4-D [4]	

[1] U.S. Department of Health, Education, and Welfare.
[2] For long-term exposures.
[3] Expressed in terms of parathion equivalent cholinesterase inhibitions.
[4] Short period limit only: 2 to 3 days, no more than once or twice a year.

TABLE 5. *Pesticide residues in fish samples from streams draining three different land-use areas, Pennsylvania—1969-71*

Collection Date	Fish	No. in Sample	Age, yr.	Residues, µg/kg				
				Aldrin	TDE	DDE	DDT	Dieldrin
Young Womans Creek (forest)								
3- 5-70	Blacknose dace [1]	47	—	0.0	0.0	32	0.0	0.0
	Northern creek chub [2]	5	1	0.0	0.0	22	0.0	0.0
	Northern creek chub	1	2	0.0	0.0	17	0.0	0.0
	White sucker [3]	4	2	TR	0.0	15	0.0	0.0
		8	3	0.0	0.0	17	0.0	0.0
Bixler Run (general farms)								
3-11-70	Blacknose dace	100±	—	0.0	8.6	31	0.0	0.0
	White sucker	10	2	0.0	4.6	16	0.0	0.0
	White sucker	10	3	0.0	0.0	23	0.0	7.1
Spring Creek Tributary (residential area)								
3-11-70	Blacknose dace	100±	—	0.0	60	350	0.0	9.0
	Northern creek chub	13	1	0.0	69	250	0.0	6.8
	Northern creek chub	18	2	0.0	50	250	0.0	7.7
	Whtie sucker	1	2	0.0	110	110	370	8.9

NOTE: TR = trace.
[1] *Rhinichthys atratulus*
[2] *Semotilus atromaculatus*
[3] *Catostomus commersoni*

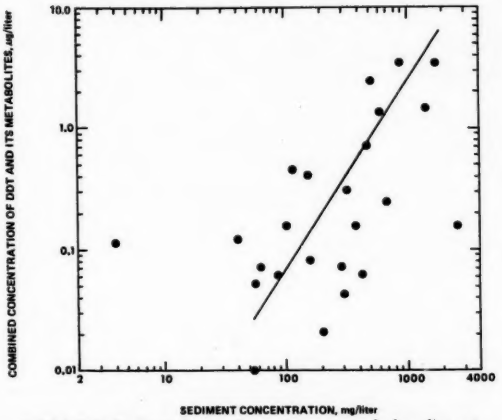

FIGURE 5. *Correlation between suspended sediment concentration and combined concentration of DDT and its metabolites in Latimore Creek tributary, Pennsylvania - 1969-71*

TABLE 6. *Particle size distribution and ΣDDT content of suspended sediment samples from Latimore Creek tributary, Pennsylvania—1969-70*

Collection Date	Sand, %	Silt, %	Clay, %	Suspended sediment concentration: Total, mg/liter	Suspended sediment concentration: Clay, mg/liter	ΣDDT, µg/liter
4-10-69	1	53	46	166	76	0.40
7-12-69	0	29	71	523	371	3.45
4- 2-70	34	46	20	482	96	0.71
6- 3-70	7	50	43	624	269	1.32
12-17-70	11	65	24	431	103	0.06

pesticide residues. These data are shown in Table 6 with the computed clay concentrations and the combined concentration of DDT and its metabolites found in corresponding pesticide samples. Except for the sample collected December 17, 1970, the concentration of DDT and its metabolites shows a better correlation with the computed clay concentration than with the total suspended sediment concentration.

Effects of Pesticides on Aquatic Life

Both the residential area and orchard streams occasionally contain temporary pesticide residue concentrations that might be toxic to some fish exposed for 96 hours (*1-3*). The maximum concentrations observed in these streams occurred during storms when suspended sediment concentrations were also at a maximum, and probably never persisted for more than a half hour. However, pesticide concentrations safe for aquatic life under continuous exposure are considerably less than 96 hours (*8*). The effects of these exposures in addition to chronic low-level exposure are practically impossible to evaluate, but it appears possible that there is occasional damage to fish populations in both the residential area and orchard streams.

Aquatic insects are more susceptible than fish to chlorinated hydrocarbon insecticides. Damage to insect populations probably occurs in both the residential area and orchard streams, because these insects spend part of their life cycles in the streambed where pesticide concentrations are higher than in the water. An attempt was made to collect fish in the orchard stream, and the streambed was examined for macroinvertebrates, but neither fish nor macroinvertebrates were found. The lack of fish food, rather than a direct fishkill, may account for the fact that no fish were found. However, pesticides may occasionally be discharged in highly concentrated slugs that could decimate both insect and fish populations. Since it is unlikely that any of the samples were collected exactly at the time of highest residue concentration, higher concentrations may have occurred.

Discussion

Pesticide residues were detected in Young Womans Creek even though none were detected in soil of the basin. Lindane was detected in all four streams but in no other environmental component. A possible explanation for this is that the detection limits for pesticides in water are lower than in other media.

Higher DDT concentrations were observed in one streambed sample and one storm runoff sample from Spring Creek tributary than in any of the samples from Latimore Creek tributary, even though DDT concentrations in the soil were much lower in the residential area drained by Spring Creek than in the orchards drained by Latimore Creek tributary. Slug discharges, possibly through the sewerage system, may account for the high concentrations. High DDT concentrations in the Spring Creek tributary may also result from storm runoff following recent applications of DDT in the residential area. No DDT has been used in the orchards for several years; thus the only source of DDT in Latimore Creek tributary is residue in orchard soils. Slug discharges of other pesticides may sometimes occur in the orchard because parts of the orchards are sprayed almost daily and summer storms sometimes occur unexpectedly, washing off recently applied pesticides.

The high DDT concentrations in soil samples from the orchards were not reflected in streambed or storm runoff samples. This suggests that most DDT remains fixed in the soil and is not easily leached. Soil that enters the streams as sediment appears to be the dominant transport mechanism of pesticide residues, indicating that effective erosion control could decrease the pesticide load in streams.

Analysis of streambed or storm runoff samples appears to be the most expedient and definitive way to determine the degree of pesticide contamination in a stream. Base flow samples contain little or no pesticide residue regardless of those present in basin soils. Fish, though they may be good indicators of pesticide contamination, are more difficult to collect and analyze.

There may be occasional damage to insect and fish populations in Spring Creek and Latimore Creek tributaries, but no water or fish samples contained pesticides above the maximum concentration for public water supplies or food fish recommended by the Public Health Service.

LITERATURE CITED

(1) *Fish and Wildlife Service, U.S. Department of Interior. 1963.* Pesticide-Wildlife Studies—A Review of Fish and Wildlife Service Investigations During 1961 and 1962. FWS Circ. 167. 109 pp.

(2) *Fish and Wildlife Service, U.S. Department of Interior. 1964.* Pesticide-Wildlife Studies, 1963—A Review of Fish and Wildlife Service Investigations During the Calendar Year. FWS Circ. 199. 130 pp.

(3) *Fish and Wildlife Service, U.S. Department of Interior. 1965.* The Effects of Pesticides on Fish and Wildlife. FWS Circ. 226. 77 pp.

(4) *Goerlitz, D. F., and E. Brown. 1972.* Methods for analysis of organic substances in water. U.S. Geol. Survey Techniques Water-Resources Inv., book 5, chap. A3. 40 pp.

(5) *Goerlitz, D. F., and L. M. Law. 1974.* Determination of chlorinated insecticides in suspended sediment and bottom material. J. Ass. Offic. Anal. Chem. 57(1):176-181.

(6) *Guy, H. P., and V. W. Norman. 1970.* Field methods for measurement of fluvial sediment. U.S. Geol. Survey Techniques Water-Resources Inv., book 3, chap. C2. 59 pp.

(7) *Public Health Service, U.S. Department of Health, Education, and Welfare. 1969.* Manual for Evaluating Public Drinking Water Supplies. PHS Pub. 1820. 62 pp.

(8) *Tarzwell, C. M. 1959.* Pollutional effects of organic insecticides. Twenty-fourth North Am. Wildl. Conf. Trans., Mar. 2-4, 1959, pp. 132-142.

RESIDUES IN SOIL

Mercury and 2,4-D Levels in Wheat and Soils from Sixteen States, 1969

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ABSTRACT

Mercury and 2,4-D levels were determined for soil and wheat from 16 States. Mercury was detected in all samples; 2,4-D was found in eight percent of the soil samples and six percent of the wheat samples analyzed.

Introduction

In 1969 wheat and its associated soil were sampled at harvest in 16 major wheat-producing States to determine levels of mercury, 2,4-D, and certain chlorinated hydrocarbon and organophosphate pesticides. Results of the mercury and 2,4-D analyses are reported here; the chlorinated hydrocarbon and organophosphate data have been published (*3*).

Materials and Methods

Wheat and associated soil were sampled from a total of 100 fields randomly selected in 16 States (Table 1). Sample sites were allocated to States and then counties in proportion to the acres of wheat grown. Each soil sample was a composite of nine cores 5.1 cm in diameter by 7.6 cm in depth spaced uniformly over a 231m² area. The sample was passed three times through a 6.3-mm mesh screen and a 2.3-liter subsample was retained and packed in a steel can for shipment. After the wheat was loaded from the combine into a truck, a composite wheat sample was collected by taking small amounts throughout the load until a 2.3-liter can was filled. Records of pesticide use during the year of sampling were obtained from growers.

Samples were sent to the Pesticides Monitoring Laboratory, Gulfport, Miss. (now located at Bay St. Louis, Miss.), where all samples were analyzed for 2,4-D on gas chromatographs equipped with electron-capture detectors. A subsample of 50 soil samples and related wheat samples were chosen randomly for mercury analyses at the Syracuse University Research Corporation, Syracuse, N.Y. The procedure used was essentially that described by Hatch and Ott (*1*).

TABLE 1. *Numbers of wheat and soil samples from sixteen States, 1969*

State	Number of Samples	
	Wheat	Soil
Colorado	4	4
Idaho	4	4
Illinois	5	5
Indiana	4	4
Kansas	22	22
Michigan	4	3
Missouri	4	4
Montana	8	8
Nebraska	8	8
North Dakota	8	8
Ohio	4	4
Oklahoma	6	3
Oregon	4	4
South Dakota	4	4
Texas	5	5
Washington	6	6
TOTAL	100	96

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TABLE 2. *Mercury and phenoxy compounds applied to sampled wheatfields of 16 States, 1969*

Compounds Applied	Percent of Farms Using Compound	Mean Application Rate, kg/ha.
MERCURY COMPOUNDS		
Ethylmercury *p*-toluene sulfonamide	10.1	0.0095
Methylmercury acetate	1.0	0.0045
Methylmercury dicyandiamide	29.3	0.0061
Methylmercury quinolinolate	1.0	0.0045
Phenylmercury urea	1.0	0.0045
All mercury compounds	42.4	0.0068
PHENOXY HERBICIDES		
2,4-D	25.3	0.2705
2,4-DB	1.0	0.0045

NOTE: Total sites sampled = 90.
Application data reported by landowners and/or operators.

Results

Pesticide use records were obtained from farmers for 99 of the 100 sites (Table 2). The phenoxy herbicide 2,4-D was applied to 25 percent of the sites at rates of 0.113 to 0.680 kg/ha., and an undetermined amount was applied to one site as a spot treatment. One wheat grower reported using 2,4-DB, a compound capable of undergoing β-oxidation in many plants to form 2,4-D (*2*).

Mercury compounds were reportedly used as seed treatments on 42 percent of the fields in amounts ranging from 0.005 to 0.01 kg/ha. active ingredient. Methylmercury dicyandiamide was the most commonly used mercury compound, followed by ethylmercury *p*-toluene sulfonamide. The reported use of mercury compounds may have been conservative, because seeds in some cases had been treated prior to purchase and the seed dressings applied were not known.

TABLE 3. *Mercury and 2,4-D levels in soil and wheat of 16 States, 1969*

	Residues, ppm dry weight					Percent of Sites with Residues	Number of Samples
	Arithmetic Mean	Geometric Mean	95% Confidence Limits		Extremes		
			Lower	Upper			
MERCURY							
Soil:							
Mercury compounds used	0.12	0.098	0.080	0.119	0.05-0.29	100.0	24
Mercury compounds not used	0.13	0.105	0.079	0.139	0.05-0.36	100.0	24
All soil samples	0.12	0.101	0.086	0.120	0.05-0.36	100.0	48
Wheat Grain:							
Mercury compounds used	0.27	0.247	0.204	0.300	0.07-0.59	100.0	24
Mercury compounds not used	0.31	0.266	0.212	0.332	0.11-1.06	100.0	25
All wheat samples	0.29	0.257	0.222	0.296	0.07-1.06	100.0	49
2,4-D							
Soil:							
Phenoxy herbicides applied	0.02	0.005	0.001	0.012	0.00-0.20	20.0	25
Phenoxy herbicides not applied	0.01	0.001 [1]	<0.001	0.003	0.00-0.75	4.2	71
All soil samples	0.01	0.002	<0.001	0.004	0.00-0.75	8.3	96
Wheat Grain:							
Phenoxy herbicides applied	<0.01	0.001	<0.001	0.004	0.00-0.05	8.0	25
Phenoxy herbicides not applied	<0.01	0.001	<0.001	0.002	0.00-0.12	5.4	74
All wheat samples	<0.01	0.001	<0.001	0.002	0.00-0.12	6.0	100 [2]

[1] Difference significant at the 5 percent level as determined by t-test of log-transformed data.

[2] Pesticide application unknown for one site.

Mercury levels in soil and grain from sites where mercury compounds had been used were not significantly different from those where no mercury was applied (Table 3). Levels of 2,4-D in soil where phenoxy herbicides had been applied were significantly higher than levels in soil from sites which received no application ($p < 0.05$). However, no significant difference was found between levels of 2,4-D in wheat from application sites and those in wheat from nonapplication sites.

LITERATURE CITED

(1) *Hatch, W. R., and W. L. Ott. 1968.* Determination of submicrogram quantities of mercury by atomic absorption spectroscopy. Anal. Chem. 40:2085-2087.

(2) *Melnikov, N. N. 1971.* Chemistry of Pesticides. Springer-Verlag, New York. 480 pp.

(3) *Wiersma, G. B., P. F. Sand, and R. L. Schutzmann. 1971.* Chlorinated hydrocarbon and organophosphate residues in wheat and soil. USDA Agricultural Research Service. ARS 81-44.

Pesticide Levels in Hay and Soils from Nine States, 1971

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ABSTRACT

In 1971 hay and soil samples were collected in 9 States to determine the incidence and levels of pesticide residues in hayfields. Residues were detected in 8 percent of the soil samples and 29 percent of the hay samples. DDT and its metabolites, DDE and TDE, were contained in 2 soil samples and 21 hay samples. Heptachlor epoxide and chlordane were detected in 1 soil sample, dieldrin in 5 soil samples, and diazinon in 4 hay samples.

Introduction

Chlorinated hydrocarbons have been the primary contaminant of animal feed in the past (*2*). Levels of these and other pesticides in hay, which is a major feed source for meat and dairy animals (*7*), is a cause for concern.

In alfalfa, pesticide residues have been found principally on the leaves and are bound to the plant cuticle (*1,2*). King et al. (*6*) found residues of heptachlor and its epoxide to be greater in the crown and roots of alfalfa plants than in the tops, suggesting year-to-year accumulation. Windblown contaminated dust, rain-splashed soil, and drift from agricultural applications of insecticides during the growing season have been suggested as possible sources of pesticide residues in this crop (*10*). Another source of residues may be the soil in which the alfalfa is grown. Beall and Nash (*3*) found evidence of DDT, dieldrin, endrin, and heptachlor translocation in alfalfa seedlings grown in five soil types. However, soil contact during harvest was not a major source of heptachlor and its epoxide in alfalfa (*6*).

The present study was undertaken in 1971 because residues of DDT, DDE, TDE, and other chlorinated hydrocarbons were detected in soil and field-collected hay samples in the National Soils Monitoring Program for Pesticides in both 1969 and 1970 (*5,11;* also Wiersma, Tai, and Sand, 1969: unpublished data). The objective of the present study was to determine pesticide residue levels associated with hay cultivation in nine States during 1971.

Materials and Methods

Soil and hay samples were collected from sites in nine major hay-producing States (Table 1). Sampling sites were allocated among States and counties in proportion to acreages of hay harvested (*9*) and were randomly distributed within counties among hayfields of 10 acres or more. A 231-m² sampling area was designated in each field. Sixteen soil cores, each 5.1 cm in diameter by 7.6 cm in depth, were collected on a uniform grid over each

TABLE 1. *Sites sampled in nine hay-producing States in 1971*

State	Hay	Soil	Hay/Soil
	Sites Sampled	Sites Sampled	Sites Sampled
Iowa	9	8	8
Kansas	7	7	7
Minnesota	10	10	10
Missouri	9	9	9
Nebraska	13	13	13
New York	6	7	6
North Dakota	12	12	12
South Dakota	10	13	10
Wisconsin	11	11	10
TOTAL	87	90	85

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231-m^2 site. The cores were composited and screened and a 2.3-liter subsample was packed in a steel can which had been rinsed with isopropyl alcohol.

Cuttings of the standing crop of hay were collected in the immediate vicinity of each soil core, air-dried, and thoroughly mixed. A 1.4-kg sample was retained for analysis and placed in a plastic bag inside a cloth bag for shipment. The types of hay sampled included alfalfa, 76 percent; mixed hay, 21 percent; clover, 2 percent; and grass, 1 percent.

In addition to the soil and crop samples, pesticide application data for the 1971 crop year, and names of any pesticides known to have been used in the previous 5 years, were obtained for each site wherever possible.

Samples were analyzed at the EPA Pesticides Monitoring Laboratory, Gulfport, Miss. (now located at Bay St. Louis, Miss.). Detailed analytical procedures are outlined by Carey et al. (*4*) for crop samples and Wiersma et al. (*11*) for soil samples. Because of possible PCB contamination of hay samples by the plastic bags which held them, PCB's were accounted for in analyses but were not considered as part of this investigation.

Results

Pesticide application data were reported by the landowners or operators for 80 of 91 sites. Only 10 percent of the respondents reported using pesticides during the 1971 crop year. The pesticides used were atrazine, chloramben, 2,4-D, diazinon, malathion, and methoxychlor. Atrazine was reportedly applied to four fields; 2,4-D to two; and chloramben, diazinon, malathion, and methoxychlor to one field each. Pesticides were applied to 30 percent of the 80 sites during the 6-year period prior to sampling.

All residues are expressed on a dry-weight basis (Tables 2,3). The data were not normally distributed, but tended to fit a log normal distribution. Thus the geometric mean was utilized to provide a better estimate of central tendency. Geometric means were calculated for the variable (x+0.01), where x is the residue determination. Adjusted geometric means are the calculated geometric means minus 0.01. Arithmetic means are also presented.

Of 90 soil samples analyzed, 8 percent contained detectable levels of pesticides. The compounds indentified were chlordane, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-TDE, dieldrin, and heptachlor epoxide (Table 1). DDTR (DDE+DDT+TDE) occurred in two soil samples, heptachlor epoxide and chlordane in one, and dieldrin in five. Organophosphates were not detected in any soil samples analyzed. The pesticides identified in hay, occurring in 29 percent of 87 samples, were *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-TDE, and diazinon (Table 2). DDTR was detected in 21 hay samples; diazinon was detected in four.

Discussion

On most sites where pesticides were detected, respondents claimed that the pesticides in question had not been applied within the six years immediately preceding sampling. Unreported use or spray drift from insecticide applications to other crops might account for some residues in hay and soil. Considering the persistent nature of the organochlorine pesticides (*8,11*), the residues detected in soil might also have originated from applications prior to 1966. In hay, other possible residue sources are translocation from the soil (*3*) and volatilization of the compounds from the soil surface with subsequent reabsorption by the cuticle of the leaves (*1,2*).

TABLE 2. *Pesticide residues detected in hayfield soils of nine States, 1971*

Compound	Residue Levels, ppm dry weight				Sites with Residues, %
	Arithmetic Mean	Adjusted Geometric Mean	95% Confidence Limits for Adjusted Geometric Mean	Maximum	
Chlordane	<0.01	*	- -	0.04	1.1
o,p'-DDE	<0.01	*	- -	0.02	1.1
p,p'-DDE	<0.01	0.001	<0.001-0.002	0.27	2.2
o,p'-DDT	0.01	*	- -	0.84	1.1
p,p'-DDT	<0.01	*	- -	0.37	1.1
p,p'-TDE	<0.01	*	- -	0.15	1.1
DDTR	0.02	0.001	<0.001-0.002	1.54	2.2
Dieldrin	<0.01	0.001	<0.001-0.002	0.12	5.6
Heptachlor Epoxide	<0.01	0.001	<0.001-0.002	0.15	1.1

NOTE: Total sites sampled = 90.
Minimum detectable level was 0.01 for all compounds.
* = Geometric mean estimate not calculated when less than two positive values were present.

TABLE 3. *Pesticide residues detected in hay from nine States, 1971*

Compound	Residue Levels, ppm dry weight				Sites with Residues, %
	Arithmetic Mean	Adjusted Geometric Mean	95% Confidence Limits for Adjusted Geometric Mean	Maximum	
p,p'-DDE	<0.01	0.001	<0.001-0.001	0.04	18.4
o,p'-DDT	<0.01	0.001	<0.001-0.002	0.05	5.7
p,p'-DDT	0.01	0.004	0.002-0.007	0.20	21.8
p,p'-TDE	<0.01	0.001	<0.001-0.002	0.03	6.9
DDTR	0.02	0.006	0.003-0.009	0.28	24.1
Diazinon	0.02	0.001	<0.001-0.003	1.32	4.6

NOTE: Total sites sampled = 90.
Minimum detectable level was 0.01 for all compounds.

The only pesticide detected in both hay and soil samples was DDTR. Of 85 hay samples, 24 percent contained DDTR residues compared with 2 percent of the 85 corresponding soil samples. This difference might be accounted for by spray drift to the hay from other fields. Another possibility is that DDTR was present in soils below the level of detection, 0.01 ppm, but was detected in the corresponding hay samples because a given weight of hay has a larger surface area available for absorption than has the equivalent weight of soil.

LITERATURE CITED

(1) *Archer, T. E. 1968.* Location, extraction, and removal of endrin residues on alfalfa hay. J. Dairy Sci. 51 (10):1606-1611.

(2) *Archer, T. E., and D. G. Crosby. 1967.* Extraction and location of selective chlorinated hydrocarbon residues in alfalfa hay. Bull. Environ. Contam. Toxicol. 2(4):191-206.

(3) *Beall, M. L., Jr., and R. G. Nash. 1969.* Crops seedling uptake of DDT, dieldrin, endrin, and heptachlor from soils. Agron. J. 61(4):571-575.

(4) *Carey, A. E., G. B. Wiersma, H. Tai, and W. G. Mitchell. 1973.* Organochlorine pesticide residues in soils and crops of the Corn Belt Region, United States—1970. Pestic. Monit. J. 6(4):369-376.

(5) *Crockett, A. B., G. B. Wiersma, H. Tai, W. G. Mitchell, P. F. Sand, and Ann E. Carey. 1974.* National soils monitoring program for pesticide residues—FY 1970. Pestic. Monit. J. 8(2):69-97.

(6) *King, R. L., N. A. Clark, and R. W. Hemken. 1966.* Distribution, movement, and persistence of heptachlor and its epoxide in alfalfa plants and soil. J. Agr. Food Chem. 14(1):62-65.

(7) *Naber, E. C., and A. C. Waldron. 1972.* Pesticide residues in feedstuffs: are they a problem? Md. Univ. Nutr. Conf. Feed Manufacturers Proc., pp. 69-72.

(8) *Nash, R. G., and E. A. Woolson. 1967.* Persistence of chlorinated hydrocarbon insecticides in soils. Science 157(3791):924-927.

(9) *U.S. Bureau of the Census. 1967.* Census of Agriculture, 1964. Vol. 1, Statistics for the States and Counties, Parts 7, 14, 15, 16, 17, 18, 19, 20, and 21. U. S. Government Printing Office, Washington, D. C.

(10) *Ware, G. W., B. J. Estesen, and W. P. Cahill. 1968.* An ecological study of DDT residues in Arizona soils and alfalfa. Pestic. Monit. J. 2(3):129-132.

(11) *Wiersma, G. B., H. Tai, and P. F. Sand. 1973.* Pesticide residue levels in soils, FY 1969—National Soils Monitoring Program. Pestic. Monit. J. 6(3):194-228.

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALDRIN	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-exo-1, 4-*endo*-5,8-dimethanonaphthalene, not less than 95%
AMIBEN	3-Amino-2,5-dichlorobenzoic acid
ATRAZINE	2-Chloro-4-ethylamino-6-isopropyl-amino-1,3,5-triazine
BHC (BENZENE HEXACHLORIDE)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CHLORAMBEN	See amiben.
CHLORDANE	1,2,3,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomeric forms of chlordane.
2,4-D	2,4-Dichlorophenoxyacetic acid
2,4-DB	4-Chloro-2-oxobenzothiazolin-3-ylacetic acid
DDE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT) *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene
DDT	Main component (*p,p'*-DDT): α-Bis(*p*-chlorphenyl) β,β,β-trichloroethane. Other isomers are possible and some are present in the commercial product. *o,p'*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane]
DIAZINON	O,O-Diethyl O-(2-isopropyl 4-methyl-6-pyrimidyl) phosphorothioate
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene
ENDOSULFAN	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide
ENDRIN	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-endo*-5,8-dimethanonaphthalene
ETHION	0,0,0',0'-Tetraethyl S,S'-methylene bisphosphorodithioate
ETHYLMERCURY *p*-TOLUENE SULPHONAMIDE	$C_{15}H_{17}HgNO_2S$
HCB	Hexachlorobenzene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
LINDANE	*Gamma* isomer of 1,2,3,4,5,6-hexachlorocyclohexane
MALATHION	S-[1,2-bis(ethoxy-carbonyl)ethyl] O,O-dimethyl phosphorodithioate
METHOXYCHLOR	1,1,1-Trichloro-2,2-bis(*p*-methoxyphenyl) ethane
METHYLMERCURY DICYANDIAMIDE	$CH_3HgNH.C(:NH)NH.CN$
PARATHION	O,O-Diethyl O-*p*-nitrophenyl phosphorothioate
PCB'S (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
SILVEX	2-(2,4,5-Trichlorophenoxy) propionic acid
2,4,5-T	(2,4,5-Trichlorophenoxy) acetic acid
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane
TOXAPHENE	Chlorinated camphene (67-69% chlorine); product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.

Information for Contributors

The *Pesticides Monitoring Journal* welcomes from all sources qualified data and interpretative information on pesticide monitoring. The publication is distributed principally to scientists, technicians, and administrators associated with pesticide monitoring, research, and other programs concerned with pesticides in the environment. Other subscribers work in agriculture, chemical manufacturing, food processing, medicine, public health, and conservation.

Articles are grouped under seven headings. Five follow the basic environmental components of the National Pesticide Monitoring Program: Pesticide Residues in People; Pesticide Residues in Water; Pesticide Residues in Soil; Pesticide Residues in Food and Feed; and Pesticide Residues in Fish, Wildlife, and Estuaries. The sixth is a general heading; the seventh encompasses briefs.

Monitoring is defined here as the repeated sampling and analysis of environmental components to obtain reliable estimates of levels of pesticide residues and related compounds in these components and the changes in these levels with time. It can include the recording of residues at a given time and place, or the comparison of residues in different geographic areas. The Journal will publish results of such investigations and data on levels of pesticide residues in all portions of the environment in sufficient detail to permit interpretations and conclusions by author and reader alike. Such investigations should be specifically designed and planned for monitoring purposes. The Journal does not generally publish original research investigations on subjects such as pesticide analytical methods, pesticide metabolism, or field trials (studies in which pesticides are experimentally applied to a plot or field and pesticide residue depletion rates and movement within the treated plot or field are observed).

Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Pesticides ordinarily should be identified by common or generic names approved by national or international scientific societies. Trade names are acceptable for compounds which have no common names. Structural chemical formulas should be used when appropriate. Accuracy, reliability, and limitations of sampling and analytical methods employed must be described thoroughly, indicating procedures and controls used, such as recovery experiments at appropriate levels, confirmatory tests, and application of internal standards and interlaboratory checks. The procedure employed should be described in detail. If reference is made to procedures in another paper, crucial points or modifications should be noted. Sensitivity of the method and limits of detection should be given, particularly when very low levels of pesticide residues are being reported. Specific note should be made regarding correction of data for percent recoveries. Numerical data, plot dimensions, and instrument measurements should be reported in metric units.

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